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CRUDE OIL SAMPLING IN SPR CAVERNS:

THE DEVELOPMENT OF AN IMPROVED PROGRAM

VIA FIELD AND LABORATORY INVESTIGATIONS

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ABSTRACT

The Strategic Petroleum Reserve (SPR), a 600 million barrel crude oil reserve stored primarily in caverns leached in Gulf Coast salt domes, is maintained by the U.S. Department of Energy (DOE). As part of a continuing program to monitor and characterize changes in the oil stored in the reserve, SPR caverns are periodically sampled at varying depths. Several different kinds of samples are withdrawn including pressurized samples, which enable a determination of the oil's vapor pressure and gas/oil ratio. parameters are particularly important to drawdown strategies because if the oil contains significant amounts of gas (therefore having a high vapor pressure and gas/oil ratio), additional equipment and decreased removal rates may be required during drawdown. Past pressurized sampling data was wrought with inconsistencies due to improper pressurized sampling and sample analysis techniques. This report documents the findings of an investigation taken to determine the source of the problems in the existing pressurized sampling and sample analysis methods and to establish reliable and cost effective methods of performing these tasks. In particular, flow-through pressurized sampling technology was found to be the most appropriate method of obtaining reliable samples. The gravity transfer method was found to be the most reliable method of moving the sample from the flow-through tool to a transportation container. In regards to sample analysis, it is recommended that gas chromatography replace the antiquated Podbielniak method, that the gas/oil ratio be measured via standard techniques rather than calculated using equations of state, and that a standard method be used to measure the sample's vapor pressure in a constant temperature PVT cell.

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INTRODUCTION

Analysis of downhole samples provides valuable information concerning the nature of the fluid at the sample depth whether drawn from oil producing wells or from oil storage caverns in the Strategic Petroleum Reserve (SPR). In particular, pressurized samples enable the vapor pressure and gas/oil ratio to be determined as a function of depth in SPR caverns. These parameters are well worth the cost and difficulty to obtain due to the limitations they place In particular, it has been established that bubble on **drawdown** strategies. point pressures larger than 50 psia at the **drawdown** temperature are likely to cause cavitation in pumps and unreliable metering. In addition, knowledge of the bubble point pressure is important enough in formulating drawdown strategies to justify determining it as accurately as possible using commercially available techniques. SPR oil composition, obtained from downhole samples, provides information concerning degradation and mixing effects as well as possible contamination from outside sources such as CH4 originating in the salt formation. Pressurized sampling is therefore a necessary part of a continuing quality assurance program.

The chief aim of this report is to discuss better methods of sampling and analyzing oil in SPR caverns. The goal is a standard, valid sampling approach for the SPR. To this end, presented in this report are the results of a comparison between alternative technology and that currently used within the SPR. This comparison includes both pressurized sampling equipment and sample analysis techniques, and is based largely on a series of field and laboratory investigations.

PRESSURIZED SAMPLING TECHNIQUES

The objective of material sampling is to obtain a representative part of a fluid or solid of interest that can be tested to determine certain physical characteristics which are representative of the bulk material from which the sample was drawn. When the sample is obtained, every effort must be made to insure that the sample is and continues to be representative of the bulk material. For example, in the case of cavern oil sampling for the determination of bubble point pressure, it is essential that the sample integrity be maintained. Thus if the sample phase separates, the analyzed sample must include both the gas and liquid portions.

In an effort to establish the best method of obtaining cavern oil samples, it is very useful to investigate remote sampling methods employed by others. Although remote sampling is widely used, the need for pressurized samples is restricted to situations where loss of sample pressure after capture is tantamount to changing the sample itself. Consequently, a thorough literature search on sampling methods revealed very few applications for pressurized sampling technology. Most sampling techniques discussed in the literature can be classified as one of two types, depending on the phase of the bulk material to be sampled. Solid samples which characterize geologic formations are obtained via downhole mechanical extraction equipment while fluid samples are generally obtained by circulating the fluid to the surface. In the case of

fluid samples, the literature abounds with various techniques of circulating potentially contaminated ground water to the surface to obtain samples. The only remote sampling technology discussed in the literature for obtaining pressurized fluid samples is found in the petroleum industry.

History of Petroleum Pressurized Sampling

The early petroleum industry concentrated on discovering and producing oil. As the industry progressed, the benefits of "bottom-hole sampling," Bottom-hole sampling provided information about the became apparent. formation and its potential as a producing oil well, as well as how to best The first pressurized tool designed to obtain down-hole data produce it. included instruments to measure pressure as well as to obtain a sample This early sampler consisted of a chamber with valves on each (Sclater 1928). end (top and bottom). The valves were in the open position during the descent of the tool and closed at the desired depth by the release of a "messenger" weight which traveled down the wireline colliding with the sampler and tripping a mechanism to close the valves. Because this type of tool exposes the sample chamber to the surrounding fluid during descent, it (and similar tools) can be classified as open-type sampling tools. A second design for a pressurized sampler was developed (Schilthuis 1935) that utilized an evacuated The vacuum was maintained during descent by two valves: sampling chamber. (1) a needle valve at the top, and (2) a check valve at the bottom in series with a replaceable tin disc. The top valve remained closed during the sampling process. By choosing the thickness of the disc carefully, one could ensure its failure at the desired depth, allowing the fluid to fill the evacuated sample chamber through the check valve. As the tool was removed, the pressure drop across the check valve due to the decreasing formation pressure relative to the pressure of the captured sample ensured a tight seal In this and similar tool designs, the sample chamber is at the check valve. allowed to contact the surrounding fluid only at the point of sampling, thus classifying it as a closed-type sampling tool.

In the years following the development of these first two tools, many tool designs were advanced, some simply refinements of previous tools and others The open-type sampler with valves tripped by a based on new designs. descending messenger was slightly refined by Exline (1937) and Lindsly (1934). Lindsly went on to produce another open-type sampler with an original valve closing mechanism (Lindsly 1936). This tool differed from its predecessors in that its top valve was closed by a mechanism which was not tripped from the surface but rather set in motion at the surface. The basic design of this tool was similar to its precursors, consisting of a sample chamber with valves on the top and bottom. However, an additional chamber was added above the top This chamber contained a spring-loaded piston which was attached to the top valve. Just prior to use, grease was injected into the chamber. grease forced the piston downward opening the top valve while compressing the The valve located at the bottom of the sample chamber was designed to move freely, closing under its own weight. After the tool was attached to the wireline, a small orifice in top of the grease chamber was opened. compressed spring pushed the piston upward against the grease which exited through the orifice at a rate dependent on the orifice size and grease viscosity. As the piston moved upward, the top valve was pulled toward its

seat. During descent, the top valve was moving slowly toward its closed position. Oil flowed into the tool through the bottom valve, up through the sample chamber and top valve, exiting through ports between the top valve and the grease chamber. When the sampler reached the desired depth it was bobbed up and down through a vertical distance of 25 to 30 ft while maximizing the velocity of the downward stroke as much as possible so that the impact of the oil on the bottom valve would open it, allowing fluid to enter and force any other oil through the top valve and out the exit ports. After this process, the tool was withdrawn with the pressure in the sampling chamber seating both the upper and lower valves.

In the following decades, similar improvements were made to open-type samplers. These improvements included clock tripped valves which closed after the tool had been **downhole** a preset amount of time (Grandstone 1941, Guerro 1959). Jar-head mechanisms which closed the valves after a snap on the **wireline** were also developed (Guerro 1959). The jerk on the **wireline** sheared a pin allowing a spring mechanism to close the valves. Closed-type sampler designs, however, still employed an evacuated sample chamber isolated from the surrounding fluid by a tin disc (Guerro 1959).

The first sampling tool which eliminated the possibility of contamination from oil incurred during the tool's descent, without evacuating the sample chamber, was one which mechanically moved or positively displaced the sample?. . into the sample chamber. This tool, described by Guerrero (1959), was designed to draw a sample into the sample chamber by a piston movement. At the surface, the tool was primed by attaching the piston directly to the wireline and locking it into position, flush against a check valve, at the bottom of the sample chamber with a piston retaining mechanism. chamber was then filled with water and several springs were bolted to the top The springs allowed the tool to descend the wellbore but of the tool. restricted its movement in the reverse direction without undue force. tool was allowed to descend to the desired depth (within the wellbore). At this point, the wireline motor was reversed. While the springs held the tool, the force of the wireline triggered the piston retaining mechanism thereby The piston was now anchored in place by the wireline releasing the piston. but not fixed to the tool. With the tool no longer fixed on the wireline, gravitational force pulled the tool down, dislodging it from the wellbore. As the tool moved downward, the piston, held at the a constant depth by the wireline, traveled the length of the sampling chamber sucking in a sample through the bottom check valve. Once this action was complete, the tool was withdrawn, the bottom check valve held shut by the high pressure in the sample In a second mode of operation, weights were attached to the tool which was then allowed to descend rapidly to the desired sample depth. this depth was released, the tool was jerked to a stop, triggering the piston retaining mechanism and allowing the piston movement to withdraw a sample. With this method the tool could be used to obtain a sample in an open hole. Success depended largely on using sufficient weight to achieve the momentum needed to provide adequate force upon deceleration to release the piston. addition, care was required to minimize jerks on the line so that the tool would not open prematurely.

Modern Sampling Technology

As discussed above, pressurized sampling technology within the petroleum industry can be classified as one of two types, open or closed. Today's openvalve samplers are much like those of the past, they are designed to descend with top and bottom valves open. Once the desired sampling depth is reached, the valves are closed by a mechanical mechanism which is tripped one of three (1) a clock, (2) a jar-head, or (3) a signal from the surface which travels through a conductor in the wireline. The current manufacturers of these tools are Ruska Instrument Corporation (Ruska) and Leutert Instruments, Inc. (Leutert). Modern closed-type samplers use either positive displacement In both cases, today's technology is essentially a refinement or evacuation. of the technology discussed above. The only positive displacement design currently marketed for sale is manufactured by Leutert (Leutert) and is loosely based on the design discussed by Guerro (1959). This tool withdraws a sample by a piston activated by either a clock or a signal from the surface. Evacuated closed-type samplers no longer rely on a tin-disc failure mechanism to expose the evacuated sample chamber to the sample fluid (like that used by Schilthuis (1935)) but generally use a surface activated motor (Microgage) which opens a valve to the evacuated sample chamber. A discussion of these tools follows.

Open-Type Sampling Equipment

Ruska's subsurface sampling equipment is available only in an open-valve configuration. Ruska offers two sizes of their Model 1200 Subsurface Sampler. Size A is available for pressures to 8,000 psi at 300°F and is able to obtain a 600 ${\rm cm}^3$ sample while size B is smaller, 400 ${\rm cm}^3$, for use to 12,000 psi at Regardless of size, the Ruska subsurface sampler is operated by 300°F. lowering it "into the well with the valves on both ends open to allow complete circulation of the reservoir fluid through the sampler." (Ruska) Once the sampling depth is reached, the tool is triggered by one of two mechanisms, a preset clock or a line-jerk. When the tool is triggered, an electromagnetic device releases a hammer (Fig. 1). The hammer falls through an air chamber striking a rupture pin which punctures a bulkhead between the air chamber and an oil chamber. The oil chamber contains a piston which is attached directly When the bulkhead is ruptured, a pressure differential to the top valve. exists between the sample chamber and the air chamber. This pressure differential moves the piston up, closing the top valve. As the top valve moves closed, a shaft attached to the sample chamber side of the top valve releases the spring-loaded bottom valve, allowing it to close. As the tool is withdrawn from the well, the pressure in the sample chamber seats both valves. The Ruska clock is available with a maximum running time of 6 hrs and can be set at time intervals in intervals of 5 minutes.

The Leutert PNL 64 open-valve sampler is much like the **Ruska** open-valve sampler, differing most significantly in the triggering and valve closure mechanisms. The **Ruska** triggering mechanism punctures a sealing disc allowing the reservoir fluid pressure to overwhelm that of an air-filled chamber thus hydraulically forcing the top valve to close. The valves on the Leutert tool are not hydraulically operated, but rather spring loaded, and allowed to close

Ruska Open-Type Sampling Tool

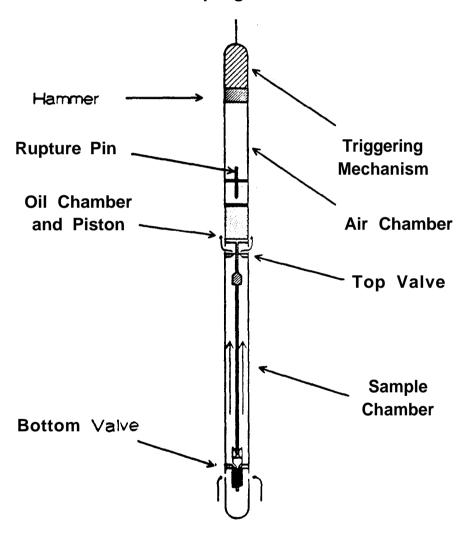


Fig. 1

when a triggering lever is activated (Leutert). The Leutert triggering lever is activated by a clock mechanism, a line-jerk, or an electric switch triggered from the surface. The Leutert tool is available in two sampling volumes, $600~\rm cm^3$ and $1000~\rm cm^3$, and has a standard pressure rating of 10,000 psi with 20,000 psi available upon request.

Closed-Type Sampling Equipment

As discussed above, closed-type sampling equipment is currently available in one of two designs, positive displacement and evacuated sample chamber. Although Core Labs of Dallas, Texas has designed and built a positive displacement tool it is only available for hire and not for sale, and will not be discussed here. At the current time, only Leutert manufactures a positive displacement tool for sale.

The Leutert 'Exal' P.D.S. System consists of two chambers, an upper reservoir chamber initially filled with air, and a lower sample chamber (Fig. 2). The two chambers are connected by a transfer tube running to the top of The lower sample chamber contains a piston which is the reservoir chamber. initially positioned at the bottom of the sample chamber, resting against the seat of a valve. This valve can be opened via a mechanism tripped by either a preset clock or a signal from the surface. The sample chamber and the transfer tube are originally filled with a buffer fluid at a given pressure. When the bottom valve is opened, the pressure differential between the fluid outside the tool and the buffer fluid, forces the piston to move up the sample This action pushes the buffer fluid up the transfer tube to the top of the reservoir chamber. Upon reaching the top of the reservoir chamber, the buffer fluid spills out into the reservoir chamber where it remains until the tool is reset at the surface for the next sample. By adjusting the viscosity and initial pressure of the buffer fluid, the sample intake rate can be regulated.

Evacuated sample chamber closed-type sampling equipment is not currently manufactured for sale by any tool companies. However, due to the simple design of these tools, many wireline companies have constructed their own evacuated sample chamber tools. In particular, Microgage Wireline (Microgage) has an evacuated sample chamber tool which consists of a sample chamber with valves on the top and bottom. The tool is prepared for use by attaching it to a motor which is connected to the wireline. The motor element has a geardriven valve which is activated from the surface via a conductor running the length of the wireline. After attaching the sampler to the motor element, the motor valve is closed, the top valve on the sample chamber opened, and a vacuum drawn on the sample chamber through the bottom valve. Once sufficient vacuum is achieved, the bottom valve is closed. The top valve of the chamber is allowed to remain open during the descent, with the evacuated sample chamber sealed by the motor valve and the bottom valve. When the desired depth is reached, the motor valve is opened and the surrounding fluid fills the evacuated sample chamber. The motor valve is then closed, and the tool retrieved. At the surface, the top valve on the sample chamber is closed and the tool removed from the motor element.

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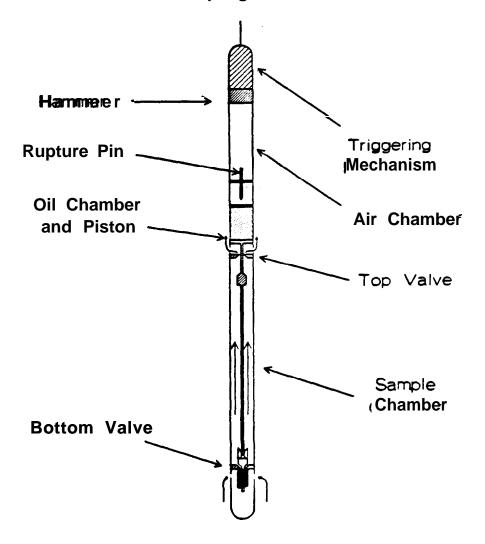


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Leutert Positive Displacement Sampling Tool

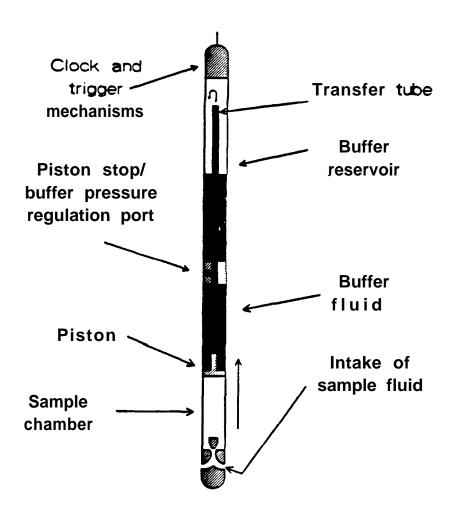


Fig. 2

Discussion of Modern Sampling Technology

Although the petroleum industry has a long history of open-valve and positive displacement tools for obtaining downhole pressurized samples, the only tool which has been used regularly in SPR caverns for pressurized samples is an evacuated sample chamber tool. In addition, cavern sampling within the SPR has been the responsibility of subcontractors who have traditionally fabricated their own tools (like Microgage). Although the subcontractor is replaced periodically, the tools are all basically the same as that described These tools are very inexpensive, but their design has two inherent First, if this type of tool is to be accurate, the vacuum drawn on the sample chamber must be high enough to preclude any significant atmospheric For the one quart samplers used in the SPR, it has been contamination. calculated that a vacuum of 29.9" Hg is necessary to restrict the contribution to bubble point error by atmospheric contamination to less than 0.3% (Linn/Heffelfinger 7/24/89). Given the field conditions often present during SPR cavern sampling, drawing and maintaining this vacuum is sometimes Indeed, when field experiments were performed to compare data from difficult. properly evacuated tools to data obtained earlier from the same cavern at the same depth, evidence of atmospheric contamination in past samples was found (Linn/Heffelfinger 7/24/89). The second inherent flaw is the possibility of a local flash occurring when the tool is opened downhole. If this were to occur, the only way a representative sample would be taken would be if both phases of the flashed oil were captured by the sampler. Furthermore, the ratio of captured flashed gas to the captured flashed liquid must be such that, once recombined in the sampler, the composition would match that of the surrounding fluid.

While evacuated samplers have two potential problems in their basic design, open-type samplers have only one, the possibility of retaining fluid during the sampler's descent. This problem was recognized by Lindsly (1934) who recommended bobbing the tool through 25 to 30 ft several times once the sample depth was reached. While this action would certainly minimize the potential for contamination, neither the retention problem itself nor the effects of the recommended solution have been quantified.

Positive displacement samplers largely eliminate the problems inherent in the evacuated and open-type designs. This design uses a pressure drop to withdraw a sample of fluid, this pressure drop can be reduced by adjusting the viscosity and pressure of the buffer fluid, thus minimizing the chance of a flash occurring during sampling. However, additional expense accompanies improved design, and increased complexity tends to decrease reliability.

SAMPLE ANALYSIS TECHNIQUES

Two methods of bubble point determination are currently used for pressurized petroleum samples: direct physical measurement and composition/equation of state determination. The first published discussion of a direct physical method was in 1935 (Schilthuis). This method, still the

basis for today's methods, involves expanding the sample from its liquid state to a two-phase state while maintaining constant temperature. The expansion is accomplished by attaching a hand operated mercury pump to the sampler. pump is essentially a piston device with which one pressurizes a supply of mercury by turning a crank. The gearing of the mechanism is such that a large movement in the hand crank is necessary to move the piston a small amount. this means, mercury is forced against the check valve until It opens. The pressure of the system is noted and more mercury forced into the sampling tool until the check valve can be held open with a valve lifter. At this point, mercury is removed until the opening pressure is re-established. To determine the bubble point pressure, the piston is withdrawn further until the pressure in the system no longer changes dramatically with slight piston movement. Once the bubble point pressure is reached, small changes in volume will induce large changes in pressure. The thermodynamic behavior of the fluid is represented by the phase diagram in Fig. 3. The process is kept isothermal by maintaining the sampler in a constant temperature bath. When the measurement process begins, the sample fluid is entirely liquid in region A. piston is withdrawn, the density decreases and the pressure drops dramatically until point B is reached. At this point, any further drop in density results in the formation of gas as the system moves into the two-phase region, region It can be seen from Fig. 3 that by monitoring the change in pressure with density (piston withdrawal), the bubble point (point B) is reached when the pressure stops changing with piston withdrawal. (Note that the process can also begin with a two-phase system (region C) which is compressed to a onephase system (region A). During this compression process, large changes in volume will result in little or no changes in pressure as the system moves toward the bubble point (point B).)

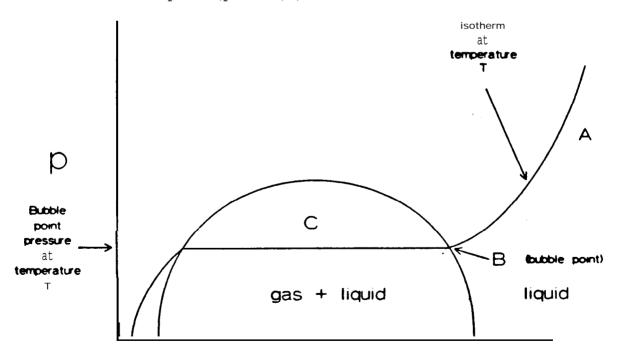


Fig. 3

The second method, composition/equation of state determination, relies on experimental techniques to determine the composition of petroleum. information is then used with an equation of state to calculate the bubble point and gas/oil ratio. This indirect method has been the method employed throughout the history of SPR sampling. The composition of the sample is determined by one of two methods: Podbielniak analysis, essentially a vacuum distillation method which requires some basic knowledge of the identity of crude oil constituents, or a complete chromatograph analysis. composition of the sample has been determined, an equation of state is used to predict the bubble point pressure as well as the gas/oil ratio at any given This analysis is but one application of the composition/equation temperature. of state tool. That is, knowing the composition and thermodynamic behavior (equation of state) of a mixture is equivalent to knowing its behavior (by calculating its thermodynamic properties) in any regime. This method is limited, however, by the inaccuracies inherent in both the compositional analysis and equation of state. Although modern equations of state are often quite reliable, repeated comparison with experimental results is necessary to refine an equation of state for a given oil.

One aim of this investigation is to quantify these inaccuracies by comparing the composition/equation of state bubble point determination method to the direct physical measurement. However, due to the vast information composition/equation of state analysis provides, it is not the objective of this investigation to study the possibility of totally replacing sample composition/equation of state analysis with a simple physical measurement of the bubble point pressure, but rather to investigate the possibility of improving the accuracy of the reported bubble point pressure of SPR samples by performing this aspect of sample analysis by direct physical measurement. Thus, even if the composition/equation of state method of bubble point pressure determination is found to be inferior to direct physical measurement, it is still useful for estimating several other quantities.

SPR SAMPLING HISTORY AND INITIAL INVESTIGATIONS

As discussed above, past SPR sampling practice has utilized only evacuated closed-type samplers to capture crude oil samples from SPR caverns. was performed by a subcontractor, most recently MicroGage Wireline. original form, this contract required the integrity of the samplers to be tested before each use. The samplers were required to be filled with water and held at a pressure of 2000 psia for 24 hours, and then examined for leaks. A field test which consisted of pumping the samplers to an unspecified vacuum and then lowering into a cavern to a point just above the oil/brine interface was also required. When the samplers were withdrawn, the vacuum was visually checked; if no oil was present, the samplers were deemed suitable for use. The contract then called for the samplers to be evacuated, again to an vacuum unspecified both in magnitude and acceptable accuracy, and used to obtain a The samples were shipped to a contract laboratory where Podbielniak analysis was used to determine the composition of the samples, $C_6{}^{\prime}s$ and below, and an equation of state was employed to obtain the bubble point pressure over a range of temperatures.

Review of Existing Data

This author first reviewed data produced by this procedure in 1988, six years after the initiation of the sampling program. The most questionable data were the opening pressures on the samplers reported by the receiving Samples obtained at deeper depths should have exhibited higher laboratory. opening pressures, however the reported pressures exhibited no trend with depth (Linn/Heffelfinger 4/24/89). In addition, the bubble point pressures for Sulphur Mines 2-4-5, which is capped by a nitrogen (N_2) layer, also exhibited no apparent trend with depth. Because of the complicated geometry of Sulphur Mines 2-4-5, mixing effects are unlikely and certainly unpredictable. Thus, one would have expected to see the reported bubble point pressure decrease with depth, representative of the decreasing amount of \aleph_2 To check the data for the possibility of atmospheric dissolved in the oil. contamination, the reported sample compositions minus the reported N_2 were used to calculate the bubble point pressures at the sampled depth. The result was a series of bubble point pressures that decreased consistently with increasing depth. In light of this analysis, it was recommended to evacuate the samplers to at least 29.6" Hg vacuum (0.01 atm) with a reliable vacuum gauge (Linn/Heffelfinger 5/15/89). The vacuum gauge used by the wireline subcontractor, a Bourdon type, was not accurate enough for this application, i.e., ± 3% of reading according to the manufacturer. If this gauge was used to measure a vacuum of 29.6" Hg and if it performed at the boundary of its stated accuracy, it may have read a vacuum of 29.6" Hg when a vacuum of only 28.1" Hg existed in the tool. This level of atmospheric contamination for the one quart sampling tool is sufficient to raise the bubble point pressure by 15% (Linn/Heffelfinger 7/24/89). Hence it was recommended that the contract not only be modified to require a 29.6" Hg vacuum to be drawn on the evacuated tools but also that the measurement of the vacuum be made with an instrument (such as a thermocouple pressure gauge) capable of accurately measuring pressure in that range (Linn/Heffelfinger 7/24/89).

Field Investigations of Atmospheric Contamination

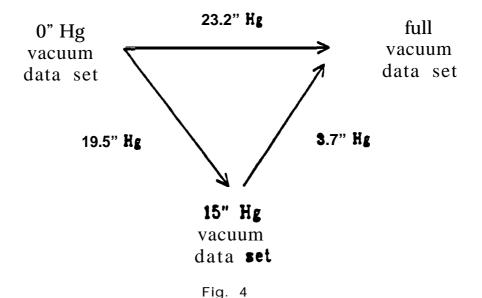
Several field investigations were performed to verify these conclusions. The objective of these investigations was (1) to certify the existence of atmospheric contamination, (2) to investigate the possibility of a flash occurring with the use of the evacuated closed-type samplers, (3) to test the results obtained using alternate sampling technology, and (4) to quantify the differences between the composition/equation of state and direct measurement methods of bubble point determination.

To certify the existence of atmospheric contamination as well as to check its effect on the bubble point pressure, two experiments were performed. In the first investigation, the routine sampling procedure was modified to include an evacuation to 29.6" Hg. The composition and bubble point pressure data were then compared to data obtained previously in the same cavern at nearly the same depth. The new sample was found to contain trace (below 0.005 mole percent) amounts of N_2 and a bubble point pressure (at 80°F) of 6 psia, as compared to the previous data for N_2 mole fraction and bubble point pressure of 0.0039 and 59 psia, respectively (Linn/Heffelfinger 7/24/89).

These results established the existence of atmospheric contamination, a conclusion affirmed by a second investigation. In the second experiment, three samples were taken from the same cavern at the same depth. The extent of evacuation was varied with one sample taken at 0" Hg vacuum (no evacuation), a second at 15" Hg vacuum (half evacuation), and a third at 29.921" Hg vacuum (full evacuation) with the measurement of the vacuum performed by the same contractor using the same equipment. An analysis of the resulting data (Linn 10/5/89) confirmed that the vacuum in the samplers was inaccurate but consistent. This conclusion is explained below.

This analysis is predicated on all samples being identical, except for the amount of atmospheric contamination. Thus the compositional analyses of the samples should be the same if the correct amount of atmospheric gas (calculated from the vacuum reportedly drawn on the 1 quart sample bottles) is subtracted. For example, if an amount of atmospheric gas equivalent to 14.921" Hg is subtracted from the 15" Hg sample, the composition should match that of the full vacuum sample. Similarly, if an amount of atmospheric gas equivalent to 29.921" Hg is subtracted from the composition of the $\bf 0$ " Hg sample, its composition should match that of the full vacuum sample, and if only 15" Hg worth is removed, the new 0" Hg sample composition should match that of the 15" Hg sample.

Once it was discovered that the data was not consistent in this respect, the calculation was reversed. Instead of subtracting the correct amount of atmospheric gas and then comparing sample compositions, the amount of vacuum which would have had to have been drawn on the sample bottle to achieve identical compositions was calculated. The results of these calculations are summarized in Fig. 4 (Linn 10/5/89).



From this figure it is seen that to arrive at the reported 15" Hg vacuum and full vacuum sample compositions from the 0" Hg vacuum data, atmospheric gas equivalent to 19.5" Hg and 23.2" Hg respectively was subtracted from the reported 0" Hg composition data. Note that these values differ from the expected values of 15" Hg and 29.921" Hg. Similarly, to arrive at the full vacuum data from the reported 15" Hg data, atmospheric gas equivalent to 3.7" Hg was subtracted, not the 14.921" Hg expected.

Once the data has been linked by calculating the atmospheric gas based differences in the data, it can be checked for consistency. From Fig. 4 we see that the data is indeed consistent. That is, the difference between the reported 0" Hq composition and the reported full vacuum composition is 23.2" Hg worth of vacuum (not 29.921" Hg as would be expected). Notice that the difference between these two compositions is the same regardless of the path If we move through the 15" Hg vacuum composition, it was calculated that we would first need to remove 19.5" Hg to get the 0" Hg composition to match the 15" Hg composition, and then another 3.7" Hg removed would get the 15" Hg composition to match the full vacuum composition. And since 19.5 + 3.7 = 23.2, we see that the full vacuum composition are 23.2" Hg from the 0" Hg composition, regardless of the path taken. This indicates that when the operator thought 15" Hg vacuum was drawn on the sample bottle, the actual vacuum was more likely 19.5" Hg and when full vacuum was thought to be drawn, only 23.2" Hg vacuum existed.

In conclusion, we can be certain that atmospheric contamination due to incomplete evacuation has been a problem in past SPR pressurized sampling. If evacuated closed-type samplers are used, their potential for atmospheric contamination must be minimized. This is possible only if a sufficient vacuum, accurately measured, is drawn and maintained on the tool. However, there remains the question of whether a flash occurs downhole upon opening the evacuated tool, and what effect, if any, this has on the sample. Consequently, a more comprehensive investigation was designed to investigate the possibility of a downhole flash occurring with the evacuated tool as well as to test the applicability of alternate sampling technology for the SPR and to quantify the differences between the compositional/equation of state and direct measurement methods of bubble point determination.

COMPREHENSIVE FIELD/LAB ANALYSIS INVESTIGATION

The initial motivation for a more comprehensive investigation of the sampling program was to ascertain whether or not a down-hole flash affected the results when using an evacuated sample. The investigation was expanded to include other types of sampling tools as well as a thorough investigation of sample analysis methods.

The objective of these experiments was two-fold. First, to define a reliable program, several aspects of pressurized cavern sampling were investigated including tool design, compositional analysis methods, bubble point pressure analysis methods, and laboratory reliability. Several

personnel witnessed the various parts of the program, and three different contract laboratories were used. The second objective was to produce reliable data on Sulphur Mines 2-4-5, the only SPR cavern with a N_2 cap. DOE has slated the Sulphur Mines site to be phased out, either by sale of the site with the oil remaining onsite, or withdrawal of the oil followed by a site sale. Thus the cavern with the highest potential for drawdown problems due to elevated bubble point is also one of the caverns slated for potential drawdown in the near future.

Structure of Investigation

The planned pressurized sampling experiments have been detailed in the experiment matrix in Table 1 below.

Depth (ft)	Evacuated Sample Chamber	Open-Valve	Positive Displacement
	E P EM	L1 L2 L3	L1 L2 L3
2459 2469 2495 2700 2950	2 2 1 2 2	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	2 2 2 4 2 2 2 2 2

Table 1: Sample Distribution

Pressurized sampling tools of three different designs, evacuated sample chamber, open-valve, and positive displacement, were used in these For the evacuated sample chamber tool, thirteen samples were experiments. taken at four different depths, 2459 ft, 2469 ft, 2700 ft, and 2950 ft. four depths were investigated due to the availability of a restricted number of tools. A single sample, SIRA (Stable Isotope Ratio Analysis), was taken at a fifth depth with an evacuated sampler at 3321 ft, slightly above the The tools employed in the study (with supplying oil/brine interface. companies) were: (1) an evacuated sampler (Microgage), (2) a Ruska flowthrough sampler (Weatherly), and (3) a positive displacement sampler (Core). The evacuated samplers were employed in three different configurations (with Table 1 reference): (1) completely evacuated (E), (2) pressurized with helium (P), and (3) completely evacuated with tool modifications (EM). In all cases, the evacuated tools were evacuated and then purged several times with helium The tool was then either to ensure the removal of all atmospheric gases. evacuated to a pressure of 1 torr (29.88" Hg vacuum) or less as measured by a thermocouple pressure gauge (E), or pressurized with helium to a pressure approximating the head pressure at the sample depth (P). By pressurizing the samplers with helium the local flash problem can be investigated. tool opens downhole, a pressure differential no longer exists, minimizing the The heavier oil should then displace the helium. By potential for a flash. comparing the sample analysis with that of other samples taken at the same depth, the extent of the flash problem can be quantified. The modified tool (EM) consisted simply of an additional tube which ran from the inlet valve on a normal evacuated sampler to $th\epsilon$ bottom of the sample chamber. This tool was

then purged and fully evacuated and used to obtain a sample. The additional tube was intended to move the location of pressure drop from outside to inside the tool, possibly eliminating sample alteration due to a local flash when the tool opens. The evacuated tool samples were analyzed by two contract laboratories, Southern Petroleum Laboratories (SPL) and Weatherly Laboratories (W).

With the other two tools, the open-valve and positive displacement, six pressurized samples were obtained at five different depths: 2459 ft, 2469 ft, 2495 ft, 2700 ft,and 2950 ft. These samples were analyzed by three contract laboratories: Southern Petroleum Laboratories (SPL), Core Laboratories (C), and Weatherly Laboratories (W).

In addition, five of the samples taken with the open-valve tool and analyzed by Weatherly Laboratories were sent to the National Institute for Petroleum Energy Research, NIPER, for further analysis. The methods and results of the NIPER tests have been compiled and discussed by Chung and Burchfield (1991) and are included in this report.

Sample Analysis Techniques Employed

Field Bubble Point Measurement

For two of the tools employed in this study, the flow-through and positive displacement samplers, a field bubble point was measured immediately upon removal of the tool from the cavern. This was accomplished for the samples taken with the flow-through sampler by attaching the tool to a hand-operated mercury injection pump (Fig. 5). Next, to insure removal of any atmospheric gas in the line, two steps were taken. First, the line between the sampling tool and the mercury pump was evacuated with a hand pump and then filled with mercury from the mercury reservoir. Next, keeping the bottom valve of the transfer bottle in Fig. 5 closed, the mercury injection pump was used to force mercury through the line between the pump and the bottom of the sampling tool and out the bleed valve connected to the bottom of the sampling tool such that the injection pump/sampling tool system was entirely mercury filled. injection pump was then operated to increase the pressure in the line until the bottom valve in the sampling tool opened, exposing the sample to the injection pump. The bubble point was then measured by removing mercury by reversing the injection pump until a two-phase system formed. amounts of mercury were then injected until the system was one-phase again. At this point the sample was moved into a mercury filled transfer bottle by the gravity method. This was accomplished by using the injection pump to fill all lines with mercury (the transfer bottle was filled with mercury in the laboratory before arriving on-site). Trapped air, if any, was removed via the bleed valves. The mercury injection pump was then used to increase the pressure in the system until it reached that in the sampling tool. point, the sampling tool valves popped open, allowing the mercury to flow downward to displace the oil in the sampling chamber, transferring it the the transfer bottle. This method precludes the use of vacuum in the transfer bottle, and if done correctly, with reliable equipment, is the best method of sample transfer available.

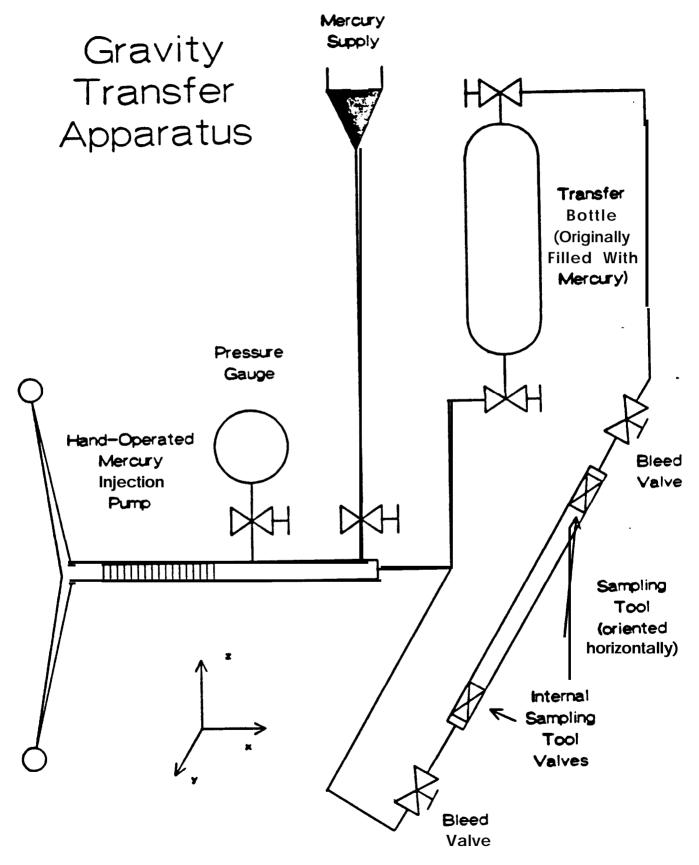


Fig. **5**

The field bubble point measurement procedure employed by the positive displacement tool contractors (Core) was quite similar, though differing in two major aspects due to differences in tool design. The design of this tool includes two chambers, separated by a piston, one for the sample and the other for the working fluid, in this case water. The first step was to connect a water pump to the working fluid chamber, increasing the pressure in this line while allowing about 600 cm^3 of sample to flow from the tool's sample chamber into an evacuated sample transfer bottle. The line between the sample chamber of the tool and the sample transfer bottle was not evacuated and varied from approximately 4" to 4' in length, depending on the operator. The sample transfer bottle was evacuated in Dallas and then transported to the site. At this point, a two-phase system existed in both the sampler and the transfer After valving off the transfer bottle, the bubble point pressure was then measured by using the water pump to force the sample in the sample chamber back to one phase.

Laboratory Analysis Methods

The three contract laboratories performed both the compositional analysis and a physical bubble point measurement on one sample at each depth. The second sample was held in reserve. The compositional analysis method depended on the laboratory. SPL and Core laboratories employed Podbielniak analysis. This is a vacuum distillation in which a sample cooled with liquid nitrogen is slowly heated allowing the components to distill off. Each component or group of components leave the system at a unique temperature, boiling off the top of the column into a previously evacuated receiver of known volume. The quantity of each component is measured by monitoring the pressure rise in the receiver. The Podbielniak results for the light ends, N_2 , CH_4 , etc. can be confirmed by further analysis of the light ends with gas chromatography. The third contract laboratory, Weatherly, flashed the sample and used gas chromatography to analyze the liquid and gas fractions of the sample.

Once the composition of the sample was determined, the contract laboratories each calculated the bubble point as a function of temperature. Like the compositional analyses, the method of calculating the bubble point pressure from the compositional data also differed between the contract laboratories. SPL employed a modified Redlich-Kwong equation of state. In their analysis, SPL arbitrarily divides the C_{7+} fraction into four equal components, C_7 , C_{11} , C_{14} , and C_7 . Weatherly used empirical correlations based on the experimental work of Lasater and Standing with California crudes, which Weatherly has adjusted to fit Gulf Coast crude. Core used experimentally determined K values reported in the Gas Producer's Association Handbook (Engineering Data Book 1957) in the usual iterative procedure.

The contract laboratories also differed on their methods of determining the solution gas/oil ratio (GOR). Both SPL and Core calculated it while Weatherly measured it directly. All of the contract laboratories included this information at three temperatures: 60°F, 100°F, and 120°F.

The physical measurements of the bubble point are accomplished as discussed above either by compressing a two-phase system to a one-phase system, as is done in the field measurements, or by expanding a one-phase

system to a two-phase system, depending on the contract laboratory. In addition, these PVT measurements can take place either in the transfer bottle (blind measurement) or a temperature controlled PVT cell equipped with a window to watch the gas fraction disappear/appear as the sample is compressed/expanded. The bubble point is the pressure at which the last bubble disappears/appears.

While the overall methods employed by the contract laboratories to measure the bubble point were much the same, they differed on details and techniques. The blind compression method depended on the contract laboratory. accomplished this by injecting water while Core and Weatherly injected In addition, the amount of gas allowed to form in the two-phase system varied widely. SPL used the blind method, injecting 10 cm3 or less, while Weatherly used anywhere from 20 to 500 cm3 in both blind and PVT cell measurements. Core used the compression method for blind measurements but expanded from one-phase to two-phase when using a PVT cell. Core's volume change in the PVT cell was generally less than 5 $\ensuremath{\text{cm}^3}$ and included only a few points in the two-phase region. Once the P-V data was obtained, SPL and Core drew a straight line though the one-phase points and another through the twophase points, reading the bubble point from their intersection. Weatherly drew a straight line through the one-phase points and a curved line through the two-phase points. This graphical method yields an estimate of the bubble point from P-V data. Another more accurate way of interpreting the P-V data is by fitting lines to the P-V data and using a Y-function analysis.

The Y-function analysis method for determining bubble points consists of plotting the calculated Y points against the corresponding pressure. The Y values are calculated from,

$$Y = \frac{P_s - P}{P (V/V_s - 1)}$$

where P_{s} and V_{s} represent the proposed bubble point pressure and volume for the recorded data. P and V are the measured data points. When performing a Y-function analysis, a P_{s} is chosen, and V_{s} calculated by linearly interpolating the P-V data. The Y points are calculated from the P and V points and plotted versus the P points. The estimated P_{s} is adjusted until a linear Y-P plot is generated. Because this method requires good data to be successful, a Y-function analysis is one measure of data quality. Although none of the contract laboratories in this study performed a Y-function analysis of their P-V data, it is possible to do so from their reported raw P_{s} V data.

The compositional analysis, bubble point measurement, and gas/oil ratio analysis methods used by NIPER on the five samples received from Weatherly Laboratories were state-of-the-art and are detailed in Chung and Burchfield's report (1991). In particular, gas chromatography was used for compositional analysis and special equipment designed for oil with low gas content was used to measure the bubble point and gas/oil ratio.

Results

The Data

A complete listing of the data has been included in Appendix I. The sample number, as assigned by BPS, is listed in the first column. The sampler number (stamped on the sample transfer bottle by the contractor) is in parentheses. Included in the data base are the field, blind, and PVT cell bubble points, the compositional analysis, and calculated bubble point profiles. Omissions in the Table represent data not collected. The NIPER results have also been included in this table, although the data field's have been modified somewhat to accommodate the uniqueness of the NIPER measurements. The corrected values of the bubble points have also been included. This was done for ease of comparison. The bubble points were corrected for temperature variations by using the calculated bubble points in the equation:

$$P^{\text{sat}}(80^{\circ}\text{F}) = \left\{ \frac{P^{\text{sat}}(T_{\text{H}}) - P^{\text{sat}}(T_{\text{L}})}{T_{\text{H}} - T_{\text{L}}} \right\} (80^{\circ}\text{F} - T1) + P^{\text{sat}}(T_{\text{1}})$$

where $P^{sat}(80^{\circ}F)$ is the adjusted bubble point pressure, $P^{sat}(T_{B})$ and $P^{sat}(T_{L})$ are the reported calculated bubble points at two temperatures, T_{B} and T_{L} , which bracket the temperature, T_{1} , of the measured bubble point, $P^{sat}(T_{1})$. The data was adjusted to $80^{\circ}F$ because most of the data was taken at temperatures at or near this temperature. This correction method is essentially a truncated Taylor polynomial, employing only the first derivative term. Because all of the reported bubble point curves (as a function of temperature) had much the same slope, this correction is only slightly dependent on which bubble point curve used. However, in an effort to maintain consistency, the bubble points were corrected using either the bubble point curves developed by one of the three contract laboratories for that particular sample or for a companion sample, taken at the same depth with the same tool and analyzed by the same laboratory.

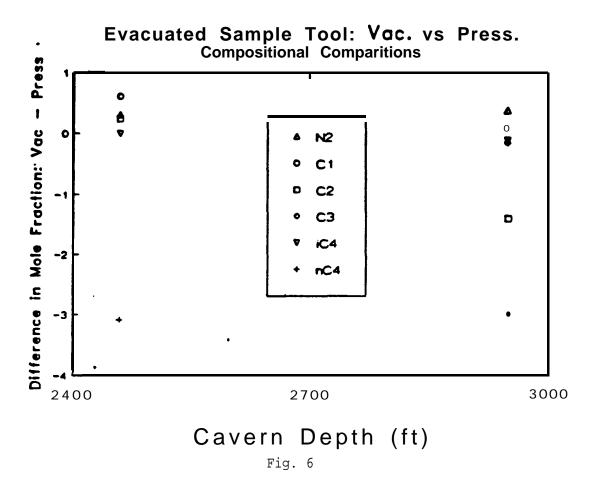
Local Flash with Evacuated Sampler

The results for the evacuated sampler, operated in two configurations: under vacuum, and pressurized with helium, are included in the data tabulated in Appendix I. In both cases, the tools were first purged with helium. When using an evacuated sampler, two types of altered samples might be found if a localized flash occurs downhole. In Case I, the oil just outside the tool might flash resulting in a loss of gas as the liquid components are sucked in. In Case II, all of the gas from the sampled oil might be sucked in with its corresponding liquid along with additional gas from flashed oil not sucked into the sampler. Case I would result in a lower reported bubble point due to reduced amounts of light ends while the Case II would result in a higher reported bubble point due to the increased amounts of light ends. Thus a plot

of the mole fractions of the light ends as a function of depth for both modes of tool operation might indicate which possibility actually occurs.

In Fig. 6 the differences in mole fractions of the five lightest components, N_2 , C_1 , C_2 , C_3 , iC_4 (isobutane), and nC_4 (normal butane), as obtained by the two methods are plotted as a function of depth. If a Case II flash is occurring when the evacuated tool is opened, two phenomena might be First, light end components should be more concentrated in the resulting sample when the sampler is evacuated than when the it is pressurized That is, for the light components (such as N_2), the difference with helium. between the evacuated and pressurized mole fractions should be larger than that of the heavier components (such as nC_4). Secondly, this effect could be more pronounced at greater depths where the potential for flash is enhanced due to the larger pressure gradient between the evacuated sample chamber and the surrounding oil. However, this might be counterbalanced by less dissolved gas at these depths. Although the data in Fig. 6 seems to indicate the occurrence of a Case II flash, one which is more severe at deeper depths, it is too scattered to allow any degree of confidence in this interpretation. However, at 2950' the trend in the mole fraction difference data for the five components appears to match the volatility of the components. possibility can be checked by plotting the mole fraction differences at this depth versus some measure of component volatility. A good measure of a component's volatility is its vapor pressure. In Fig. 7 the mole fraction differences have been plotted against the component vapor pressures. vapor pressures were calculated by Nath's equation for vapor pressure (Walas Unfortunately, the data is too scattered for any firm conclusions, however, the mole fraction difference between the two methods generally increases with component volatility. The logarithm of the bubble point has been used merely to facilitate the plotting of all of the data; there is no theoretical justification for this procedure.

Perhaps the most reliable method of investigating the effect of evacuating the sampler is to plot the sum of the light end mole fractions as a function of depth for the two methods. This reduces the relative magnitude of the errors inherent in the individual component mole fractions. If a Case II flash has occurred the combined mole fractions of the light ends should be higher for the evacuated samples than the pressurized samples. This data has The fact that the combined mole fractions of the been plotted in Fig. 8. light ends is larger for the evacuated samples than the pressurized samples at all depths where data is available, provides evidence of the occurrence of Case II flash with evacuated samplers. This plot also indicates that severity of the flash is less at greater depths. One possible explanation for this phenomena might be that the capture of stray bubbles is less pronounced at greater depths due to the increased density of the oil. In addition, if we believe that the pressurized operation of the evacuated sampler provides reliable data, this figure would indicate that the amount of gas dissolved in Sulphur Mines 2-4-5 increases with depth. This conclusion is not only contrary to conventional wisdom given the presence of the N_2 cap and limited potential for convective circulation of the oil but it is not supported by similar data from the flow-through and positive displacement tools (discussed in the following text).

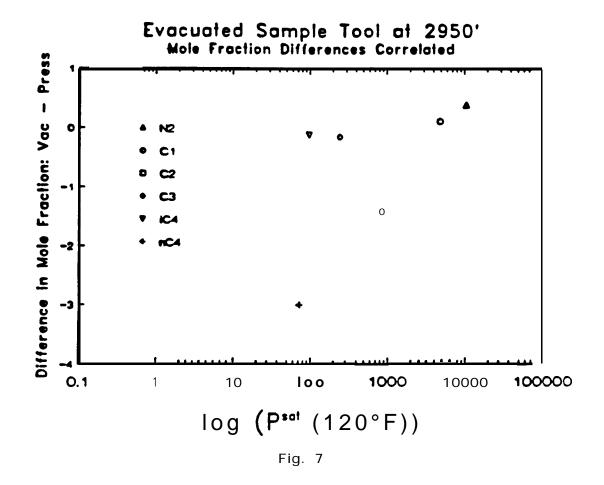


Bubble Point for Sulphur Hines 2-4-S

Methods: Compositional/Equation of State

In an effort to compare the calculated and measured bubble point pressures, the percent difference (at 80°F) between the calculated and measured bubble points has been plotted es • function of depth for the bubble points reported by each of the three contract laboratories in Figs. 9, 10 and 11. By comparing these figures it is clear that, of the three contract laboratories, Core's calculated bubble points match their measured bubble points most closely. In addition, the spread in the Core data is the smallest of the thret contract laboratory data sets.

Core's calculated bubble points are themost likely to fit SPR oil. This is dut to the fact that their method tmploys neasured parameters (K values) for unspecific crudes. Weatherly's correlation should bt next liktly to fit SPR oil. While it employs measured parameters, these have btan fit to a specific crude, Gulf Coast, whereas SPR oil is a mixture of many different crudes. SPL's method of calculating the bubble points from the compositional data is the most general, and therefore is liktly to deviate the most from the txptrimtntally measured bubble points.



Evacuated Sample Tool: Vac. vs Press.
Compositional Comparisiont

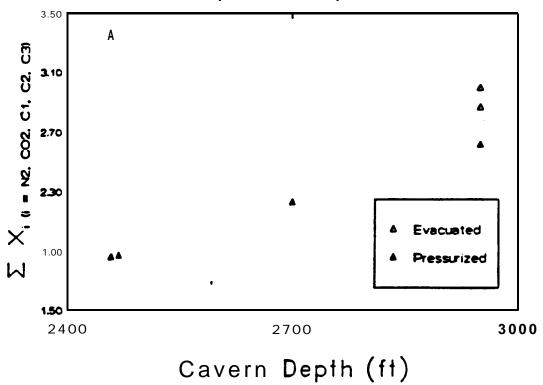
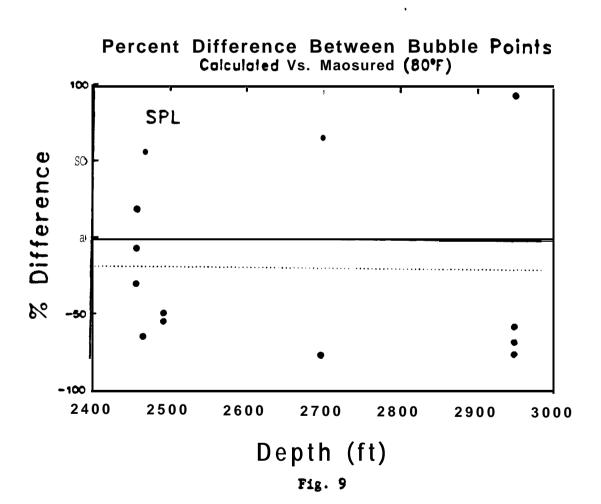
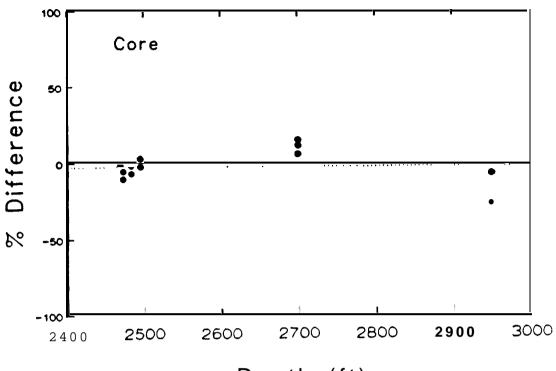


Fig. 8

These observations can be numerically confirmed by calculating the percent difference between the calculated and measured bubble points and determining the standard deviation of the data. The average deviations are -2.5%, -14.6%, and -18.9%, for Core, Utathtrly, and SPL, respectively. The dotted lines on Figs. 9, 10 and 11 represent these averages. The standard deviations of the reported data are 11.4, 34.4, and 59.0, for Core, Utathtrly, and SPL, respectively. Thus the deviations of the calculated bubble points from the measured bubble points art much as expected. SPL's general method is least accurate, and Core's method, based on measured parameters for unspecific oil, is most • ccuratt. However, these observations provide no insight as to the quality of the compositional analysis performed by the contract laboratories. The compositional analysts will be discussed more fully below.



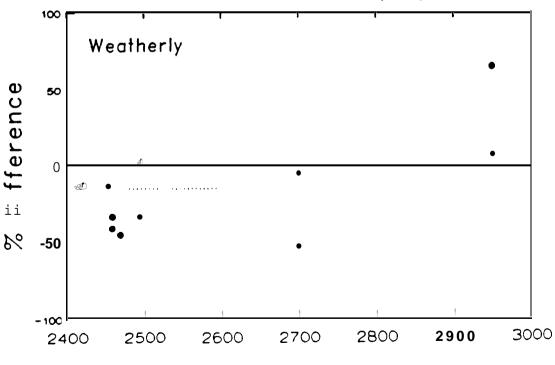
Percent Difference Between Bubble Points Calculated Vs. Measured (80°F)



Depth (ft)

Fig. 10

Percent Difference Between Bubble Points Calculated Vs. Measured (80°F)



Depth (ft)

Fig. 11

Methods: Direct Measurement

Although the same basic techniques were used in this investigation to measure bubble points, the measurement techniques differed slightly, contract laboratory to contract laboratory. Therefore, in addition to comparing calculated and measured bubble points, we can also compare measured bubble points as determined by variations of the same basic technique. accuracy of the bubble point measurement depends many factors. equipment used to make the measurement is perhaps the most obvious factor. This equipment varied from field equipment to laboratory measurements in blind cells to laboratory measurements in carefully controlled PVT cells, in order from least to most accurate. Variations in the basic measurement technique as well as in the methods of interpreting the P-V data play an important part in the accuracy of a measured bubble point. For example, compression measurements do not always produce results which match those produced by expansion measurements. In both cases, the AV used to make the measurements The volume changes employed in the physical bubble point is important. measurements in this work varied from 1 cm^3 to 500 cm^3 . These and other factors governing the accuracy of bubble point measurement are discussed below in the context of the data generated by this investigation.

Using large $\Delta V's$ when making bubble point measurements is essential to producing reliable P-V data for two reasons. The first is due to equipment and operator based measurement errors. Measurements of large changes in volume and pressure minimize the relative magnitude of errors introduced by The second is the fact that during the either the equipment or the operator. bubble point measurement process, the P-V measurements are made in a changing When the system is two-phase, either emerging from a one-phase system via a volume expansion or moving toward a one-phase system via a compression, the two-phase system compressibility is controlled mainly by the gas phase. However, in the transition from one-phase to two-phase (expansion) or from two-phase to one-phase (compression), the system's compressibility becomes increasingly dependent on the dominant phase: the gas phase if the system is being expanded, and the liquid phase if the system is being compressed. transition of the system compressibility is gradual and causes the curve in the P-V data near the bubble point. Therefore, it is essential to obtain data well into the one- and two-phase regions, minimizing the percent of data that is taken in the curved region where the system's compressibility is ambiguous. Using smaller $\Delta V's$ is faster but yields P-V data concentrated in the curved region of the P-V curve. This data is not only more difficult to interpolate graphically, but is also less reliable. In Figs. 12 and 13, P-V data for two extremes of AV used during this investigation have been plotted. From Fig. $12\,\text{,}$ P-V data using a AV of about 1 $\text{cm}^3\,\text{,}$ the graphical interpolation difficulties are immediately apparent. However, any thermodynamically based inconsistencies or systematic errors are not obvious from this data. interpolation of P-V data can proceed a number of ways, as discussed above. The correct way to graphically interpolate the P-V data is to plot the P-V data and draw a curved line through the two-phase points and a straight line through the one-phase points, reading the bubble point pressure as the pressure coordinate of the point of intersection. The use of one straight line and one curved line is appropriate because the equipment used in these analyses is not sufficiently accurate to pickup the slightly nonlinear

SPL Per Measurement at 2459' $\Delta V = .56 \text{ cm}^3$

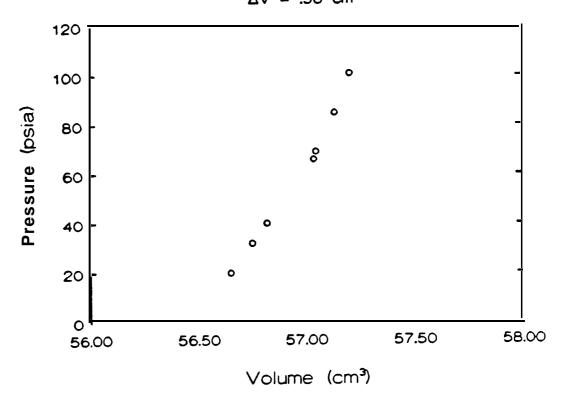


Fig. 12

Weatherly P^{min} Measurement at 2459' $\Delta V = 485 \text{ cm}^3$

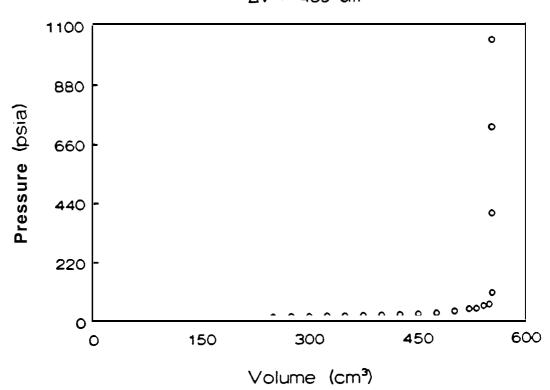


Fig. 13

behavior of the one-phase compressibility but it is accurate enough to record the slightly nonlinear behavior in the two-phase region. The intersection of these two lines is an <u>estimation</u> of the bubble point. This estimation can be improved by one of two numerical methods: fitting a curved line to the two-phase data and a straight line to the one-phase data and then numerically interpolating the ordinate of their intersection, or a Y-function analysis. While curve fitting the points improves the accuracy of the graphical interpolation method, a Y-function analysis is no more difficult and provides a more accurate bubble point with additional information about the consistency of the data. Therefore, a Y-function analysis is a more appropriate method of interpreting P-V data to produce a bubble point.

Another consideration in evaluating the reliability of the reported measured bubble point data is the method of measurement. The PVT cell expansion method of measuring the bubble point pressure is less reliable than the PVT cell compression method because the expansion method is much more operator dependent. When expanding the liquid oil, it is possible for the operator to move the system beyond its bubble point pressure and not be aware of it. Once the system pressure drops below this point, microbubbles will form throughout the liquid. The operator must take the time to allow these bubbles to migrate to the top of the cell where a visible bubble will form. Thus the speed at which the expansion method is conducted significantly affects the results. This is not to say that the two methods won't give the same results, but rather that the compression method is more reliable.

None of the contract laboratories performed a Y-function analysis on their P-V data (it was not specified in the contract). Both Weatherly and SPL ascribed to the view that a Y-function analysis was worthwhile, especially for P-V data from PVT cells. Core Laboratories, on the other hand, didn't feel that a Y-function analysis was worthwhile for such low bubble points. That is, very good data, sufficient to yield a linear Y-P plot, was likely to be too difficult to obtain given the fact that low bubble points increase the relative magnitude of measurement errors. In order to investigate (1) the usefulness of a Y-function analysis for low bubble point oil, and (2) the possibility of obtaining more accurate interpretations of P-V data for the measured bubble point results, this author performed a Y-function analysis on the available P-V data.

Unfortunately, little data gathered from this investigation lends itself well to Y-function analyses. This may indicate that a Y-function analysis is not worthwhile for oil with low bubble points, however, it may also be due to the small $\Delta V's$ used to obtain the P-V data, operator errors, or measurement inaccuracies which are large relative to the magnitude of the measurements of the volume and pressure changes. The wide range in $\Delta V's$ employed can be seen in Fig. 14. In this figure, the deviation of the reported measured bubble point pressure from that obtained from a Y-function analysis, expressed in percent, has been plotted against the AV used in the P-V measurements. All of the bubble point measurements (and therefore Y-function analyses) were made at or near $80^{\circ}F$, except the additional PVT cell measurements made by Weatherly at a range of temperatures: $70^{\circ}F$, $95^{\circ}F$, $110^{\circ}F$, $125^{\circ}F$, and $140^{\circ}F$. The points with a zero difference are not actual data points but rather represent points which produced no sensible Y-function bubble point. Therefore, points on the

abscissa indicate that the reported bubble point pressure is based on P-V data that is inconsistent with a Y-function analysis. From this figure, we see immediately that the amount of data above AV - 100 cm³ is insufficient to support any conclusions. However, for the data with AV less than 100 cm³, it is easily seen that a P-V data obtained using a smaller AV data was much less likely to yield • sensible Y-function bubble point. That is, as AV &creases we see more points on the abscissa, especially for AV < 50 cm³.

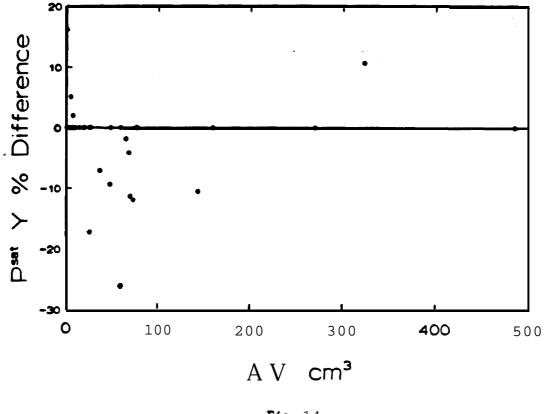


Fig. 14

Direct Measurement Results

The measured bubble points can also be compared on a tool-by-tool basis. After correcting the results to 80°F by the method discussed above, the bubble points have been plotted vs depth for the tools employed. This has been done in three separate plots (Figs. 15, 16, 17) for each of the three measurements taken: field bubble points, bubble points taken in blind cells, and bubble points taken in PVT cells. Three features are immediately seen in Fig.15, the field bubble point plot: (1) the bubble point decreases with depth, (2) the data at 2700 ft is widely scattered, and (3) the scatter in the flow-through tool's results is less than that of the positive displacement tool. The blind and FVT cell bubble point plots (Figs. 16 and 17) confirm thetrend with depth and scattered data at 2700 ft, however, the differences between the precision of the flow-through snd positive displacement tools are not as apparent from these plots. This can be seen more clearly from Figs.18, 19,

and 20, which correspond to Figs. 15, 16, and 17, but have an adjusted scale enabling a closer look at the scatter in the data.

Weatherly also performed a PVT cell measurement of the bubble point as a function of temperature. These results have been plotted in Figs. 21, 22, 23, 24, and 25. The bubble point should monotonically increase with temperature, but it is clear from these figures that experimental error plays a large part in PVT cell measurements. These errors are most likely due to using a small AV and/or a small sample. However, a physical explanation for possible decreases in the bubble point pressure with increased temperature, has been advanced by Brian Sonnier of Weatherly Labs. According to Sonnier (Sonnier, 1990), this phenonomena is sometimes seen with oils containing large concentrations of undissolved alphaltenes. These heavy components appear to exist in the oil as pseudo-solids and affect the bubble point only at higher temperatures where they melt and mix with the oil, having a net effect of lowering the bubble point. While this may be a plausible explanation for the strange bubble point-temperature relationship observed, it is more likely due to experimental error, especially since the errors appear random rather than systematic. Before anything can be said about plausible explanations for SPR bubble points which decrease with increasing temperature, better data must be obtained.

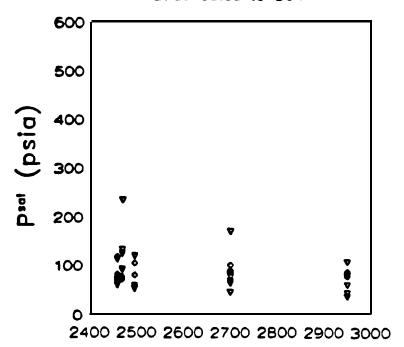
Gas/Oil Ratio (GOR) for Sulphur Mines 2-4-5

As we have seen from the calculated bubble point, using compositional data to calculate thermodynamic properties of SPR oil (such as bubble point pressure and GOR) is a science in its infancy. Therefore, the only reliable GOR's from this investigation are those physically measured (by Weatherly Laboratories). Consequently, while both the calculated and measured bubble points have been tabulated in Appendix I, only the measured GOR's have been plotted in Fig. 26. In addition, straight lines have been fit to the data, with the solid line representing the positive displacement tool data and the dotted line the flow-through tool. Keeping in mind that these results are somewhat operator dependent, we can see from this figure that the GOR decreases with depth. Also, like the field measured bubble points, the spread in the data from the flow-through tool is less than that of the positive displacement tool. A nominal result for the GOR of the oil in Sulphur Mines 2-4-5 is 7 • 10 SCF/BB1 (std conditions: 1 atm and 60°F).

Specific Gravity

Another parameter of interest is the specific gravity of samples drawn at different depths. This data has been plotted in Fig. 27 for the different sampling tools used in this study. The data does not appear to depend on which tool was used to obtain the sample. More importantly, the oil shows no signs for density stratification, therefore mixing effects in Sulphur Mines 2-4-5 are unlikely.

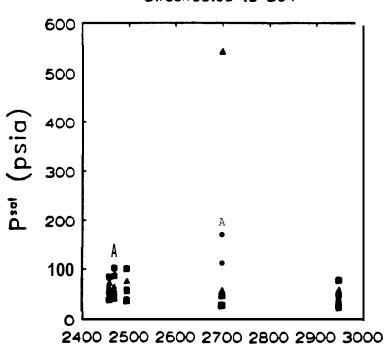
Field Bubble Points at/corrected to 80°F



Donth (44)

Depth (ft)

Blind Bubble Points at/corrected to 80°F

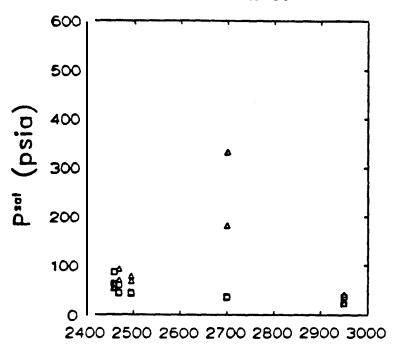


- Bind
- Bind

Depth (ft)

Fig. 16

PVT Cell Bubble Points at/corrected to 80%

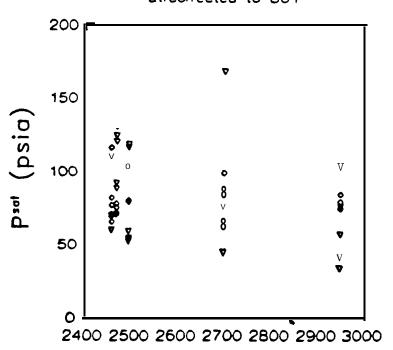


Depth (ft)

Fig. 17

Field Bubble Points at/corrected to 80%

Pos-Diso Field Flow-Through



Depth (ft)

Fig. 18

Blind Bubble Points at/corrected to 80%

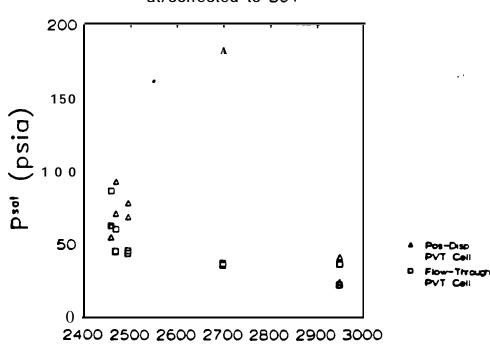
50

2400 2500 2600 2700 2800 2900 3000

Depth (ft)

Fig 19

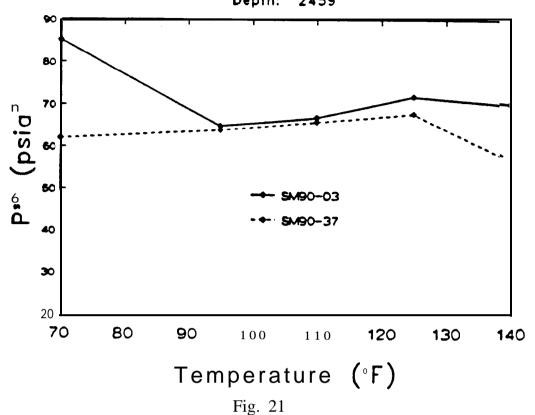
PVT Cell Bubble Points at/corrected to 80°F



Depth (ft)

Fig. 20

Weatherly Lab PVT Cell Bubble Point Data Depth: 2459'



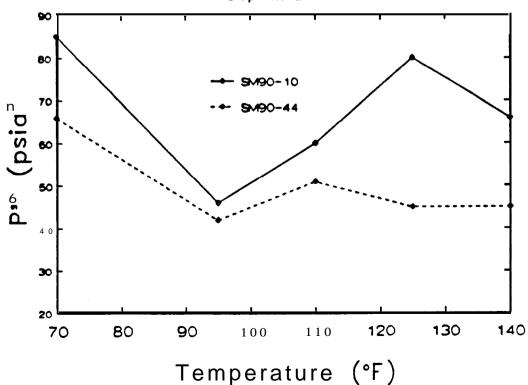
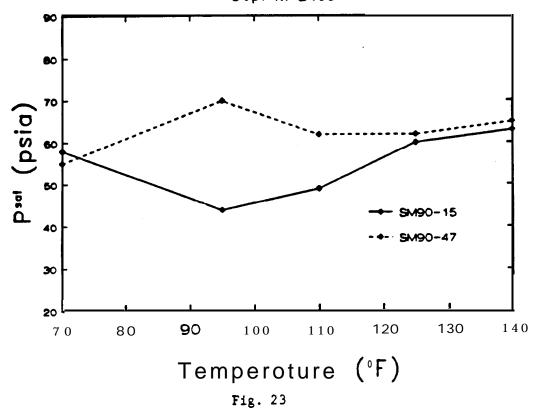


Fig. 22

Weatherly Lab PVT Cell Bubble Point Data



Weatherly Lab PVT Cell Bubble Point Data Depth: 2700'

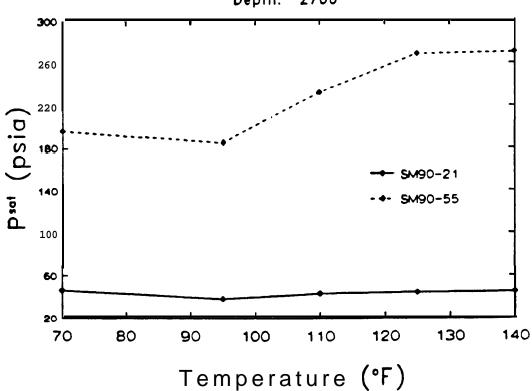
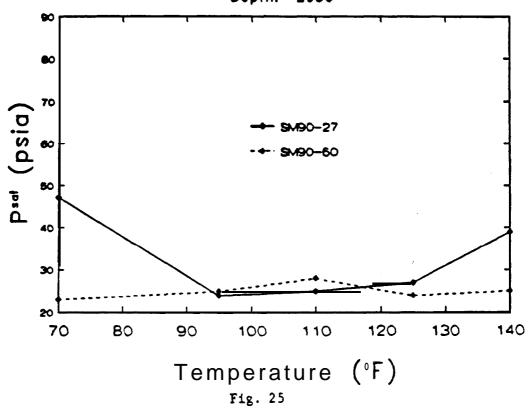
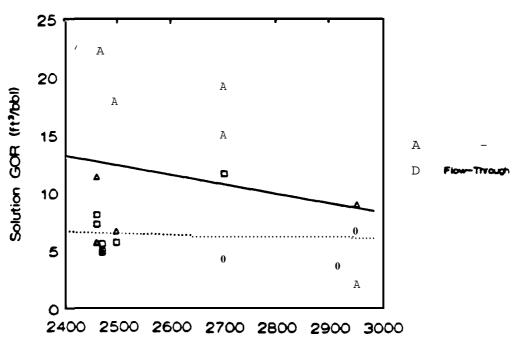


Fig. 24

Weatherly Lab PVT Cell Bubble Point Data Depth: 2950'



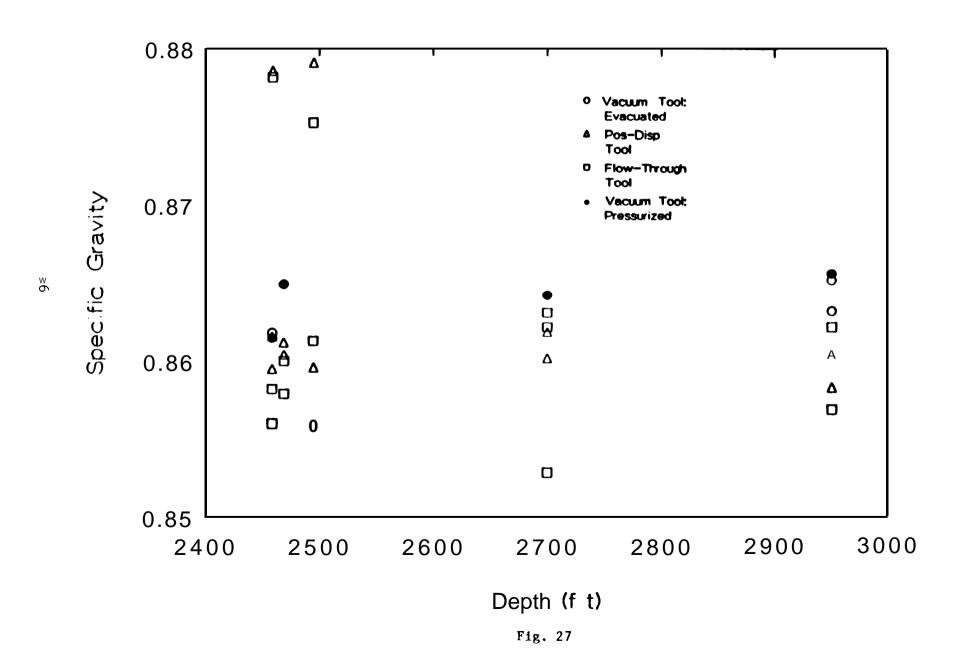
Measured Solution GOR's for Two Tools: Flow-Through vs Positive Displacement



Depth (ft)

Fig. 26

Sample Specific Gravity



A Comparison of Compositional Results

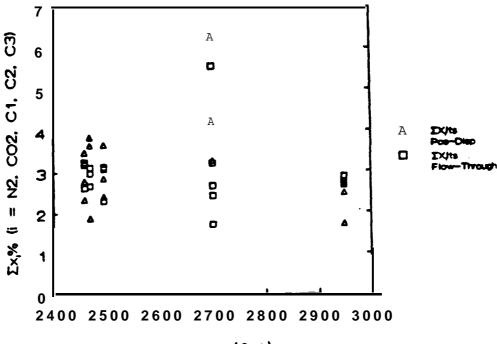
The compositional results can be compared between tools much the same as reported bubble points (Figs. 15, 16, and 17). To reduce the scatter in the data, the sum of the reported mole fractions of several light components, N,, CO_2 , C_1 , C_2 , and C_3 , has been plotted vs depth for the positive displacement and flow-through tools in Fig. 28. This figure supports the conclusions of the analogous bubble point comparisons in several ways. First, we see scatter in the data at 2700 ft. Second, the summed mole fraction of the light ends appears to decrease with depth, which supports the evidence for bubble points which also appear to decrease with depth. Third, at the three shallowest depths (2459 ft, 2469 ft, and 2495 ft), it can be seen that the data produced by the flow-through sampler (at these depths) is less scattered than that produced by the positive displacement sampler. This concurs with the data presented in Fig. 15, the plot of field bubble points vs depth for the different tools. This data does not, however, match that of the evacuated tool operated pressurized with helium, plotted in Fig. 8. Thus it must be concluded that while operating the evacuated tool pressurized with helium may prevent a downhole flash, the results of this method are not consistent with the results of the flow-through and positive displacement tools.

To compare the compositions reported by the different contract laboratories and to reduce the scatter in the data, the sample compositions have been lumped into four components: $N_2 + CO_2$, $C_1 + C_2 + c$, C_4 's + C_5 's, and C_6 's + C_{7+} , and plotted vs depth in Figs. 29, 30, 31, and 32. In addition, the the data for each contract laboratory (excluding all data taken at 2700 ft) has been curve fitted to a straight line, also shown in the figure. From these figures we see several trends. In support of previously discussed data, the summed mole fraction of the light ends: N_2 , CO, C, C_2 , and C_3 , decreases with increasing depth and the composition data from samples at 2700 ft is widely scattered. In addition, it can be seen from these figures, especially Fig. 29, that the reported mole fractions of the light ends are consistently higher for Podbielniak data than for data obtained by gas chromotography. Podbielniak analysis has been known since the 1950's to have problems accurately determining N_2 , C_1 , CO, as well as other light end species (Preston, 1957).

CONCLUSIONS

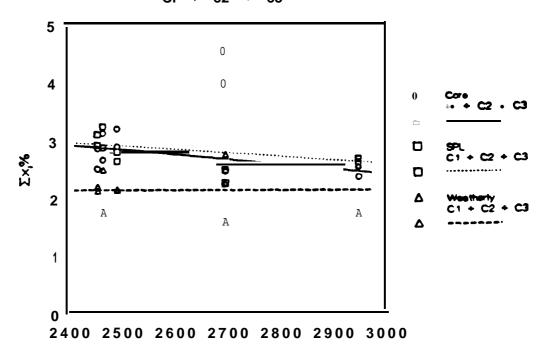
Obtaining consistent data for samples drawn from SPR caverns, at least Sulphur Mines 2-4-5, is obviously difficult. However, data from a second generation sampling program will help quantify the problem. Based on the conclusions drawn from this investigation, a number of recommendations can be made concerning: (1) the method of obtaining and transferring samples, (2) the contract laboratory analysis methods, including bubble point and compositional analysis, and (3) several other issues such as contract specifications.

Compositional Comparisions Pos-Disp vs Flow-Through Tools



Depth (f t)
Fig. 28

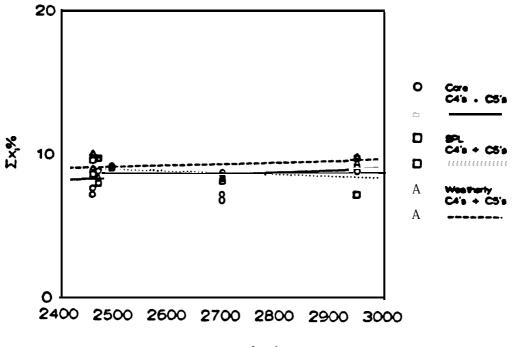
Compositional Comparisions Between Labs CI + c2 + c3



Depth (ft)

Fig. 29

Compositional Comparisions Between Labs



Depth (ft)

Fig. 30

Compositional Comparisions Between Labs C6's + C7+

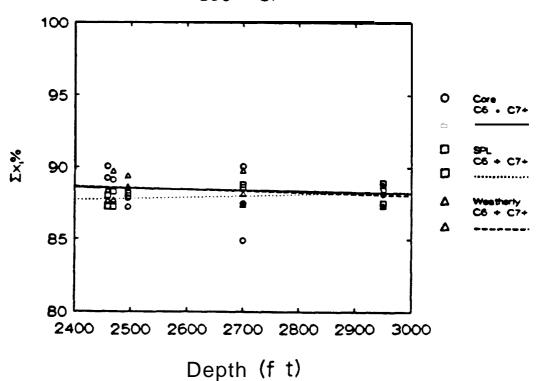


Fig. 31

Compositional Comparisions Between Labs N2 + CO2

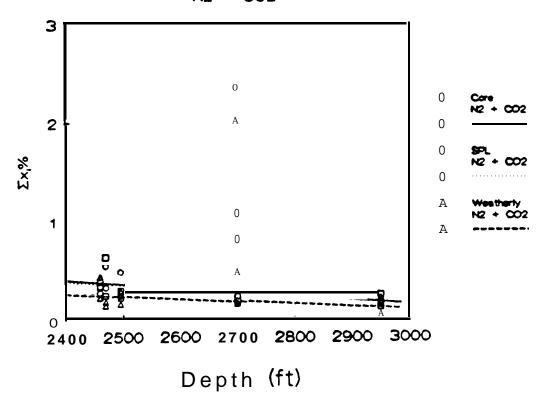


Fig. 32

40

(1) Cavern Sampling Methods

Although evacuated tools are cheaper to design and build, their design is fundamentally flawed. Even if it were possible to insure that an effective vacuum was maintained when using these tools, the results would still be affected by down-hole flashing. Operating the tools in a pressurized mode in an attempt to prevent the flash does not improve accuracy of the results. In addition, the data from the evacuated tool modified with the intake tube provided no evidence that this modification was an improvement. A good tool design is one that is not only fundamentally sound in its physical design, but also one that is simple, reliable, and minimizes the amount of attention to details required by its operators. The evacuated tool fulfills none of these requirements.

With the evacuated tool ruled out, the flow-through and positive displacement tools must be compared. The flow-through sampler yielded more consistent field measured bubble points and light end compositions, regardless of the contract laboratory analysis method, as well as more consistent measured GOR's. While precise data (reproducible data) is a desirable characteristic of sampling tools, several issues should be explored before basing tool selection on this basis alone. Because the precision of SPR cavern samples is affected by at least two factors: (1) the tool design and the way it may or may not interact with the oil at the sampled depth, and (2) and the sample transfer method, the possibility of obtaining data that is precise but not an accurate representation of the oil at the sampled depth must be considered.

Because the flow-through tool is open when it enters the cavern, it is possible that the tool will retain oil as it descends. This is not to say that this significantly affects the results but that the extent of this effect has never been quantified. This weakness may contribute to the precision in the data from samples obtained with this tool. For example, if significant amounts of oil is retained during the tool's descent into a cavern containing oil that is stratified and locally homogeneous, the data might very well be unscattered but not representative of the oil at the depth at which the tools This same cavern would yield different results if sampled with valves closed. a positive displacement tool. The positive displacement sampler would produce equally unscattered results, although they may differ from those obtained by the flow-through sampler. On the other hand, if the oil were unstratified and locally inhomogeneous, a flow-through tool which retained significant amounts of oil during its descent would provide data which was unscattered only because the tool would have sampled a larger body of fluid (albeit vertically and not because the oil at the sampled depth was actually oriented), In this case, the scatter in the data from the positive homogeneous. displacement tool would probably be greater due to the nonhomogeneity of the oil at the sampling depth. In summary, by itself the scatter in the data is not a criteria which provides sufficient basis for selecting pressurized sampling tools for SPR caverns. This conclusion is based largely that the fact that the amount of spacial nonhomogeneity of the oil stored in SPR caverns is largely unknown.

As data precision should not be used as the sole basis for tool selection, several other comparisons between tools and sampling methods must augment comparisons of data precision when selecting sampling tools for caverns in the SPR. Moreover, it is likely that the precision of the sampling tools used in this investigation is due to sample transfer methods rather than considerations of tool design. As discussed above, the sample transfer methods used in this investigation were tool-specific. The sample transfer process for the positive displacement tool was designed to use the tool's intake piston to push the sample into a transfer bottle. For this technique to work, the transfer bottle and connecting lines must be fully evacuated. Core evacuated the transfer bottle (in Dallas) but did not evacuate the connecting line. However, the vacuum drawn on the transfer bottles was not recorded either in Dallas or before use in the field. The transfer process used with the flow-through tool was the gravity method which minimizes the use of vacuum to remove atmospheric contaminants. Thus, at the current time, the However, gravity transfer processes gravity transfer process is superior. Concern for the environment was partly the invariably employ mercury. motivation for the development of positive displacement technology. Therefore, any decision concerning SPR sampling tools and sampling methods must consider not only cost and quality, but also environmental risk.

Considering the cost and quality, the flow-through sampler is the tool of choice for sampling SPR caverns. The positive displacement tool was difficult to use, expensive, and unreliable. In particular, the design of this tool employees extensive use of O-rings which are difficult to use and, unless used The flow-through tool's chief weakness is the fact carefully, unreliable. that the potential for oil retention during the tool's descent is as yet However, this problem can be minimized if the tool is bobbed vigorously once it has arrived at the sampling depth. Naturally, bobbing the tool result in samples representing a range of depth rather than specific Although this may seem restrictive in light of past sampling practice, where caverns have been sampled in 10 ft. intervals, the only sample depth which needs to be taken at a specific depth is the SIRA sample (Stable Isotope Ratio Analysis) which is used in biodegradation studies. although the SIRA sample does not require a representative amount of light ends and thus could be taken with an evacuated tool, it is probably more efficient to use one type of sampler for all samples. The bobbing technique should be used with the flow-through tool to obtain pressurized samples from 3-4 regions in the cavern, sufficient for cavern bubble point and gas/oil ratio characterization. The environmental concerns of the gravity transfer method are best dealt with by employing a reliable contractor experienced in the use of mercury for gravity transfers of pressurized samples. the sampling program should remain open to the introduction of alternate technology.

Finally, once the effort has been made to obtain representative samples, the samples should be checked in the field to ensure that a sample has actually been obtained. This could be accomplished cheaply by measuring the weight change of the sampler. A second way of checking for a sample would be to measure the bubble point in the field. Although this is more expensive than weighing, it is probably cost effective since much of the equipment needed perform a field measurement of the bubble point is required for sample

transfer anyway. In addition, to increase the accuracy of the field bubble point measurement, the sampler should be allowed to remain at the sample depth for a time sufficient to allow it to equilibrate to the oil's temperature. After withdrawal, the field bubble point measurement should be made before the sample has a chance to change temperature. Finally, the temperature of the oil and opening pressure of the tool should be taken before measuring the field bubble point measurement.

(2) Laboratory Analysis Methods

Compositional Analysis

Although bubble points determined by direct measurement are more accurate than those determined via compositional/equation of state analysis, the latter provides a wealth of other relevant information. Therefore direct measurement of the bubble point is recommended to supplement compositional/equation of state analysis of SPR pressurized samples. Accurate bubble point data for oil contained within SPR caverns is not only valuable in the event of a **drawdown** but immensely useful in the ongoing quality assurance program within the SPR, a goal of the original sampling program.

Once a data base of reliable experimental bubble point data has been established, it may be worthwhile to develop refined equations of state for SPR oil, perhaps on a cavern-by-cavern basis. These equations could be used to predict a number of thermodynamic parameters for a given cavern, bubble point included. However, the development of these equations of state would require more detailed compositional analysis. For example, the effect of lumping the C_{7+} fraction, which composes approximately 80% of a typical SPR cavern sample, has been calculated to change the results of the calculated bubble point pressures and gas/oil ratio by at least 10%. Therefore, an improved sampling program should employ chromatographic analysis which is not only able to report composition beyond C_7 , but also is more accurate for light end composition.

Bubble Point and GOR Analysis

At the current time, very little reliable bubble point or GOR data is available for the SPR. This problem is best remedied by implementing an improved sampling program which employs reliable sampling and sample analysis techniques including physical measurement of bubble points in visual PVT cells and measured GOR's.

Using a visual PVT cell does not ensure accuracy; good experimental technique must be used. The PVT cell measurement should be conducted using the compression method (moving a two-phase system to a one-phase system by compressing it). The sample size should be at least 200 cm^3 with an initial gas cap large enough to require a compression of at least 200 cm^3 to force the gas cap into the liquid. The system must be sufficiently equilibrated between volume changes before the pressure is recorded. Finally, not only should the visual bubble point pressure (pressure at which the last bubble of gas cap disappears and the system is entirely one-phase) be reported but also the bubble point pressure as obtained from graphical interpolation of the P-V data

and that calculated from the Y-function analysis of this data. The contract laboratory report should also include the raw P-V data and calculated Y-function values for each temperature with: (1) the plot of pressure vs. volume used to graphically interpolate the data, and (2) plots of Y vs P used to determine the bubble point pressure from the Y-function analysis. A proposed specification for this measurement along with sample data and contract laboratory report has been included in Appendix II.

The temperature of the PVT cell bubble point measurement should be chosen carefully. The most useful bubble point data would be at the temperature of the oil during drawdown as it reached the surface pumps and meters. However, the drawdown temperature of SPR caverns varies widely because of varying cavern depths and the existence of some annular hanging strings. Therefore it would be most useful to measure the bubble point pressure at two temperatures, establishing upper and lower limits. Two temperatures which would be the general upper and lower limits for SPR oil drawdown temperatures are 95°F and 140°F.

(3) Anomalies at 2700 Feet

Throughout this investigation, data from samples taken at 2700' was widely scattered. The scatter was not confined to a certain tool, contract laboratory, or even the day of sampling. This is strong evidence that the oil at 2700' in Sulphur Mines 2-4-5 is much different from that at other depths. This can only be confirmed with more data, from improved sampling and sample analysis procedures. The likelihood that the anomalies at 2700' occur because of unusual mixing effects due to the cavern's taper just above this point (one proposed explanation) is unlikely based on the lack of density stratification apparent from Fig. 27.

(4) Contract Specifics and Other Recommendations

One of the key components of the sampling program is reproducibility. Because no reliable data currently exits to allow comparison with past results for consistency, it is recommended that, during the implementation phase of the revised sampling program, three samples be taken per depth each time a cavern is sampled. Two should be analyzed and compared while the third should be held in reserve until it is certain that the results from the two analyzed are consistent and reliable. Once it has been established that the new sampling procedures are reliable, this requirement may be relaxed. The three sample depths should be consistent for each cavern, with samples drawn at the top, middle, and bottom (just above the oil/brine interface). middle samples should be cavern specific, that is, each cavern's top and middle samples should be withdrawn at the same depth each time. the samples at constant depths within a given cavern, compositional changes with time may provide insight as to geologic effects, such as CH, intrusion and convective circulation. Due to the movement of the oil/brine interface caused by brine removal necessitated by creep closure, the bottom sample depth will vary from sampling to sampling.

The contracts for the improved sampling program should extend only until the new program has been further revised and accepted with confidence. These contracts should then be extended to five years to allow the contractors to concentrate on quality and efficiency. Also, due to the exacting nature of pressurized cavern sampling requirements, it may be beneficial to bid the pressurized cavern sampling contract separately from the unpressurized.

Several additional useful pieces of information can be generated during the sampling process if a little extra work is done. For example, in addition to the temperature and opening pressure of the tool, recorded in the field, it would be useful to know the temperature and pressure of the sample transfer bottle in the field before transfer and upon arrival in the contract laboratory. The field opening pressures should be checked for consistency with depth (deeper samples should have higher opening pressures). In addition, the pressure of the sample bottle in the field should be compared to that in upon arrival in the contract laboratory. These pressures will not be the same due to the difference in temperature, but this enables groups of samples, all undergoing the much the same temperature change, to be compared. This is one method of spotting sample loss during transfer.

Finally, for ease of comparison, all bubble points should be recorded in psia, at temperatures in ${}^{\circ}F$. Some contract laboratories report pressure in psig which creates needless confusion.

IMPLICATIONS FOR THE STRATEGIC PETROLEUM RESERVE

Perhaps the most important reason to maintain a pressurized sampling program for the SPR is to inspect the reserve oil for gas contamination. Certain SPR caverns are known to lie in salt domes containing indigenous This gas may leak into SPR caverns, dissolving in the oil. methane gas. Excess gas in the oil on drawdown can cause problems such as inaccurate metering of oil flow, pump cavitation and drawdown equipment damage, and sinking roofs in floating roof tanks at receiving terminals. In addition, Sulphur Mines 2-4-5 has a nitrogen cap overlying the oil, a known source of gas contamination. Regardless of the origin of the gas, whether from the salt formation or from a gas cap on top of the oil, knowing the extent of gas intrusion as a function of depth not only enables economically acceptable mitigation strategies, especially for drawdown planning, but also gives some indication of the nature of the gas source (if geologic) and convective mixing, caused by salt dome thermal gradients. Thus a reliable sampling program, one which is continually updating the bank of data concerning SPR oil quality and drawdown viability, is an essential part in maintaining SPR readiness.

APPENDIX I.

Comprehensive Field/Lab Analysis Investigation Data Base

SOLUTION GAS-OIL RATIO ★

SAMPLE NUMBER	CYLINDER NUMBER	DEPTH FEET	MEASURED GAS-O RATIO	CALCULATED GAS-OIL RATIO
90-05	WLC046	2459	8.1	3.6
90-03	WLC013	2459	7.3	•••
90-37	CORE 13130E	2459	5.7	1.2
90-38	CORE 13118E	2459	11.4	• • •
90-10	WLcoo4	2469	5.6	1.5
90-12	WLco47	2469	5.0	•••
90-44	CORE 13146	2469	4.9	0.6
90-43	CORE 13111E	2469	22.3	
90-15	WOC042	2495	5.7	1.2
90-17	WLC012	2495	5.7	* * *
90-47	CORE 30A	2495	6.7	2.4
90-48	CORE 13138E	2495	17.9	•••
90-21	WLC142	2700	4.3	0.3
90-23	wLco29	2700	11.61	7.6
9 0-55	CORE 59DS633	2700	19.2	15.1
90-56	CORE 57DS1283	2700	15.0	• • • •
90-27	W116	2950	6.6	1.2
90-29	w149	2950	3.6	
90-57	CORE 349112D	2950	2.0	0.0
90-60	CORE 349164D	2950	8.9	• • •

^{*} GAS-OIL RATIO =
TOTAL SOLUTION GAS/BBL. STOCK TANK OIL AT 15.025 PSIA & 60°F

SPR Sulphur Mines 2-4-S Pressurized Sampling

	Field Contractor	: MICROGAGE	Tool Type: E	EVACUATED SAMPLER	
ANALYTI CAL LAB: SPL	FI ELD BP	"BLINO" BP	PVT CELL BP	CALWLATED BP (EOS)	COMPOSITION
SM90-62 (B-20) (Values Corrected to 80°)) a •	64.8 a 80° 64.8	9 •	50.9 a 0'F 60.0 a 80°F 53.1 a 20°F 62.6 a 100°F 55.6 a 40°F 65.3 a 120°F	N2-0.36 n-C4-3.01 C02-0.10 i-C5-2.3 CH4-0.65 n-C5-2.54
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:	0.00			57. 6 a 60°F 68.3 a 140°F 71.0 a 160°F	C2-0.45 C6-6.0 C3-1.78 C7+-82.4 i - U- 0. 75 H2S-0.0
FIELD COMMENTS: VAC 29.9	9 psia				
\$\\\\90-64 (8-22) (Values Corrected to \\\80^*)) a •	\$ •	a ,	8.4 3 0'F 11.9 3 80°F 9.0 a 20°F 13.3 a 100°F 9.8 3 40°F 15.0 3 120°F	N2-0.06 n-U-3.21 C02-0.03 i-CS-2.1 CH4-0.05 n-C5-2.7
klc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:	0.00			10.8 a 60°F 17.0 3 140°F 19.3 a 160°F	C2-0.22 C6-4.9 C3-1.50 C7+-84. 1-C4-0.76 H2S-
FIELD COMMENTS: Ne 8 1362	peia				
ANALYTICAL LAB: WEATHERLY	FI ELD BP	MBLIND" BP	PVT CELL BP	CALWLATED BP (EOS)	COMPOSITION
SM90-63 (8-21) (Values Corrected to 80°)	•	97.0 a 70° 98.2	§ •	a 0°F	N2-0.29 n-C4-2.4 CO2-0.04 i-C5-2.0 CH4-0.43 n-C5-3.4
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grrvity:				a 60° F a 140°F a 160°F	C2-0.29 C6-8.2 C3-1.24 C7+-81. i - Cl - 0.60 H2S-
FIELD COMMENTS: VAC 29.9	9 psia				
SWO-65 (B-23) (Values Corrected to 80°)) a ·	⑤ ●	a •	a 0'F a 80°F a 20°F a 100°F a 40°F a 120°F	N2-0.03 n-CL-2.1 C02-0.02 i-C5-2.(CH4-0.13 -n-C5-3.1
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grevity:				a 60°F a 140°F	C2-0.18 C6-8.(C3-1.04 C7+-82. i-C4-0.55 H2S-
FIELD COMMENTS: Ne 8 1362	psia				
	Field Contractor:	LUGE	Tool Type:	POSITIVE DISPLACEMENT 700	
ANALYTI CAL LAB: CORE	FIELD BP	"BLI ND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
\$\text{\$\frac{1}{2}\text{\$\frac{1}\text{\$\frac{1}{2}\text{\$\frac{1}{2}\text{\$\frac{1}{2}\text{\$\frac{1}{2}\text{\$\frac{1}{2}\text{\$\frac{1}{2}\text{\$\frac{1}{2}\text{\$\frac{1}{2}\text{\$\frac{1}\text{\$\frac{1}\text{\$\fin}\text{\$\fin}\text{\$\frac{1}\text{\$\fin}\text{\$\fin}\$\fin	60. 0 2 AMB *	276. 7	3 •	a 0'f a 80'f a 20'f a 100'f	N2- n-CL- CO2- i-C5-
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:				a 40°F a 120°F a 140°F a 160°F	CH4- n-C5- C2- C6- C3- C7+- 1-C4- H2S-
\$M90-34 (873832-B) (Values Corrected to 80°)	70.0 a AMB*	45. 7 a 70° 47. 2	54.7 a 80° 54.7	38.0 a 0'F 49.0 a 80°F 40.0 a 20°F 52.0 a 100°F 43.0 a 40°F 55.0 a 120°F	N2-0.20 n-C4-2. C02-0.07 f-cs-1. CH4-0.46 n-CS-2.
klc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:				46.0 a 60-f 59.0 a 140°F 63.0 a 160°F	C2-0.41 C6-5. C3-1.64 C7+-84 1-C4-0.66 H2S-0.
ANALYTICAL LAB: SPL	FI ELD BP	™BL I ND"BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
\$M90-35 (13139-EF) (Values Corrected to 80°)	60.0 a 89° 59.0	ত •	© •	© 0'F a 80°F a 20°F & 100°F 8 40°F & 120°F	: N2- n-C4- CO2- i-C5- CH4- n-C5-
klc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grevity:				a 60°F a 140°l 8 160°F	
\$M90-36 (13012-E) (Values Corrected to 80°)	110.0 a 77°) 110.4	73.7 a 78' 74.0	§ •	41. 2 3 0' F 51. 5 3 80° F 43. 6 3 20° F 54. 5 3 100° F 46. 1 3 40° F 57. 6 3 120° F	N2-0.24 n-C4-2. C02-0.14 i-CS-2. CH4-0.77 n-CS-3.
				46 I M NUT 3/ D = 120 r	U#4*U.// II-∪3-3.

BPR Sulphur Nines 2-4-S Pressurized Sampling

]	Field Contractor	: CORE	Tool Type:	POSITIVE DISPLACEMENT TOO	
ANALYTICAL LAB: WEATHERLY	FI ELD BP	mBring. Bb	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-37 (13130-E) (Values Corrected to 80°) Calc GOR (SCF/bbl): 1 Measured GOR (SCF/bbl): 5 Sample Specific Grrvity: (1. 20 5. 70	8 •	62.0 9 70° 62.5	36.0 8 0' F 42.0 a 80° F 36.0 8 20° F 43.0 a 100° F 39.0 8 40° F 45.0 a 120° F 41.0 8 60° F 47.0 8 140° F 48.0 8 160° F	M2-0.19 n-c4-3. C02-0.03 -i-85-2. CM4-0.34 n-c5-3. C2-0.29 C6-8. C3-1.49 C7+-78 i-U-Q.71 M2S-
\$M90-38 (13110-E) (Values Corrected to 80 Calc GOR (\$CF/bbl): 0 Measured GOR (\$CF/bbl): 1 Sample Specific Grrvity:). 00	62.0 a 70° 62.5	a •	a 0'F a 80°F a 20°F a 100°F a 40°F a 120°F a 60°F a 140°F a 160°F	N2- n-U- CO2- i-C5- CH4- n-C5- C2- C6- C3- C7+- i-C4- H2S-
J	Field Contractor:	WEATHERLY	Tool Type:	RUSKA FLOW THRU TOOL	
ANALYTICAL LAB: CORE	FIELD BP	"BLI ND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
(Values Corrected to 80°) Calc GOR (SCF/bbl): 1 Neasured GOR (SCF/bbl): 0 Sample Specific Grevity: 0	64. 6 13. 24). 00	52.7 a 70° 54.7	61.7 a 76° 62.5	46.0 a 0'F 59.0 a 80°F 49.0 a 20°F 63.0 a 100°F 52.0 a 40°F 66.0 a 120°F 55.0 a 60°F 71.0 a 140°F 75.0 a 160-F	M2-0.25 n-U-2.5 CO2-0.08 i-C5-1.7 CH4-0.55 n-C5-2.1 C2-0.46 C6-5.4 C3-1.85 C7+-83. i-U-0.76 M2S-0.0
SM90-08 (WLC-023F) (Values Corrected to 80°) Calc GOR (SCF/bbl): 0 Measured GOR (SCF/bbl): 0 Sample Specific Gravity:). 00	51. 7 a 70° 53. 7		© 0°F	CO2 i-C5- CH4- n-C5-
ANALYTI CAL LAB: SPL	FIELD BP	' BLI ND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-06 (Y-203) (Valuer Corrected to 80° Calc GOR (SCF/bbl): 5 Measured GOR (SCF/bbl): 0 Sample Specific Grevity: 0	5. 83 0.00	9 •	a •	37.8 a 0'F 46.1 a 80°F 39.7 a 20°F 4B.6 a 100°F 41.7 a 40°F 51.4 a 120°F 43.6 a 60°F 54.4 a 140°F 57.7 a 160°F	N2-0.25 n-C4-3.4 i-c5-2.2 CH4-0.53 n-C5-3.0 C2-0.47 C6-5.5 C3-1.92 i-C4-0.78 N2s-
SM90-07 (W-5B) (Values Corrected to 80°) Calc GOR (SCF/bbl): 0 Measured GOR (SCF/bbl): 0 Sample Specific Grrvity:	0.00	37.9 a 72° 3B.9	ଡ •	9 0'F a 80° F a 100° F a 100° F a 120° F a 140° F a 140° F	N2- n-CC- CO2- i-C5- CH4- n-C5- C2- C6- C3- C7+- i-C4- H2S-
ANALYTICAL LAB: WEATHERLY	FIELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-03 (VLC-013) (Values Corrected to 80°) Calc GOR (SCF/bbl): 0 Measured GOR (SCF/bbl): 7 Sample Specific Grevity:	0.00	ତ •	*84° \$ 70° 86.0	© 0°F a 80°F 8 20°F a 100°F 8 40°F a 120°F 8 60°F a 140°F 2 160°F	*N2- n-C4- CO2- i-C5- CH4- n-C5- C2- C6- C3- C7+- i-C4- H2S-
Calc GOR (SCF/bbl): 3 Weasured GOR (SCF/bbl): 6 Sample Specific Gravity: 0	3.60 3. 10	84.0 a 70° 84.0		43.0 a 0°F 51.0 a 80°F 45.0 a 20°F 53.0 a 100°F 47.0 a 40°F 54.0 a 120°F 49.0 a 60°F 56.0 a 140°F 58.0 a 160°F	N2-0.39 n-C4-2.8 C02-0.04 i-C5-2.0 CH4-0.44 n-C5-3.4 C2-0.33 C6-7.2 C3-1.42 C7+-81. i-C4-0.64 H2S-

		Field Contracto	r: WEATHERLY	Tool Type: RUBW FLOW THRU TOOL		
ANALYTI CAL	LAB: WI PER	FI ELD BP	NIPER BP		COMPO	SITION
SM90-05	(WLC-046)	68. 0 3 76'	65. 4 9 72°		N2-0.26 CO2-0.03 CH4-0.29 C2-0.10 C3-0.15	n-C4-0.07 i-C5-0.02 n-C5-0.02 C6+-0.03
Measured	GOR (SCF/bbl)): 5. 17			1-64-0.03	H2S-

Field Contractor: MICROGAGE

SAMPLE DEPTH 2469

Tool Type: EVACUATED SAMPLER

ANALYTICAL LAB: SPL	FIELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-66 (B-24) (Values Corrected to 80°) Calc GOR (SCF/bbl): 0 Measured GOR (SCF/bbl): (Sample Specific Grrvity: (). 14 0.00	. ⊕	॒ ●	3.5 a 0'F 7.5 a 80°F 4.2 a 20°F 9.1 a 100°F 5.2 a 40°F 10.8 a 120°F 6.2 a 60°F 12.9 a 140°F 15.3 a 160°F	N2- CO2-0.03 i-C5-2.2 CH4-0.13 n-C5-3.(C2-0.26 C6-5.6 C3-1.45 C7+-83. i-C4-0.69 H2S-
FIELD COMMENTS: Ne a 1379					
SN90-70 (B-1?) (Values Corrected to 80°)	a •	⊙ •	69 •	© D'F 8 80°F 8 20°F 8 100°F 8 40°F a 120°F	N2· n-CC- CO2· i-C5- CH4· n-C5·
Calc GOR (SCF/bbl): (Measured GOR (SCF/bbl): (Sample Specific Gravity:				a 60°F a 140°F a 160°F	C2- C6- C3- C7+- 1-C4- H2S-
FIELD COMMENTS: VAC a 29.9	psia				
ANALYTICAL LAB: WEATHERLY	FI ELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-67 (B-25) (Values Corrected to 80°)	ə ·	9	69 •	a 0°F	N2-0.03 n-C4-2.5 C02-0.03 i-Cs-2.1 CH4-0.20 n-E-3.5
Calc GOR (SCF/bbl): 0 Measured GOR (SCF/bbl): 7 Sample Specific Gravity:				a 60°F a 140°F a 160°F	C2-0.24 C6-9.C C3-1.21 C7+-80. i-cl-0.60 H2S-
FIELD COMMENTS: He a 1379 g	psia				
I	Field Contractor	r: CORE	fool Type:	: POSITIVE DISPLACEMENT TOO	
ANALYTICAL LAB: CORE	FI ELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
\$M90-39 (13142-E) (Values Corrected to 80°)	90.0 a 93' 87.4	135.7 a 93° 133.1	a •	a 0°F a 80°F a 20°F a 100°F a 40°F a 120°F	N2- n-U- CO2- i-C5- CH4- n-C5-
Calc GOR (SCF/bbl): (Measured GOR (SCF/bbl): () Sample Specific Gravity:				a 60°F a 140°F a 160°F	
\$M90-40 (13135-E) (Values Corrected to 80°)	120.0 a 77° 120.6	89.7 a 70° 91.7	91.7 a 77° 92.3	74.0 a 0'F 91.0 a 80°F 78.0 a 20°F 95.0 a 100°F 8.0 a 40°F 100.0 a 120°F	N2-0.42 n-U-3.0 cot-o.12 i-C5-1.9 CH4-0.81 n-C5-3.0
Calc GOR (SCF/bbl): 1 Measured GOR (SCF/bbl): 0 Sample Specific Gravity: (0. 00			87. 0 a 60°F 105. 0 a 140°F 110. 0 a 160°F	C2-0.46 C6-6.4 C3-1.85 C7+-81. i - h- 0.76 H2S-
ANALYTI CAL LAB: SPL	FI ELD BP	"BLI ND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
\$M90-41 (992266-C) (Values Corrected to 80°)	130.0 a 77° 130.5	⊙ •	69	© 0'F a 80° F a 20° F a 100° F	
Calc GOR (SCF/bbl): (Measured GOR (SCF/bbl): 0 Sample Specific Gravity:				a 40° F a 120°F a 60° F a 140°F a 160°F	CH4- n-C5- F C2- C6- C3- C7+- 1-C4- H2S-
\$890-42 (289440-D) (Values Corrected to 80°)	125. 0 3 85 • 124. 7	58.7 2 78° 59.0	ග •	77.9 a 0°F 91.9 a 80°F 81.5 a 20°F 95.5 a 100°F	N2-0.49 n-CC-Z. 1 CO2-0.14 i-CS-1.9 CN4-1.34 n-C5-3.2
Calc GOR (SCF/bbl): 1 Neasured GOR (SCF/bbl): C Sample Specific Gravity: C	0.00			85.0 a 40°f 99.0 a 120°f 88.5 a 60'F 102.7 a 140°f 106.5 a 160°f	C2-0.48 C6-7.1 C3-1.41 C7+-81. i-C4-0.54 H2S-
ANALYTI CAL LAB: WEATHERLY	FI ELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-43 (13111-E) (Values Correctad to 80°) Calc GOR (SCF/bbl): 0	0.00	a •	8 •	9 0°F 9 80°F 9 20°F 9 100°F 9 40°F 9 120°F a 60°F a 140°I	N2- n-CC- CO2- i-C5- CH4- n-C5- F C2- C6-
Measured GOR (SCF/bbl): 2 Sample Specific Grrvity:				a 160°F	C3- C7+- i-C4- H2S-

	Field Contractor:	CORE	Tool Type:	POSITIVE DISPLACEMENT TOO	
ANALYTI CAL LAB: WEATHERLY	FIELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
a(Values Correctedió) o 8 Calc GOR (SCF/bbl) Measured GOR (SCF/bbl) Sample Specific Gravity:	0.60 4.90	66.0 a 70°	70.7 a 66°	35.0 a 20°F	CO2-0.03
	Field Contractor	: WEATHERLY	Tool Type:	RUSKA FLOW THRU TOOL	
ANALYTICAL LAB: CORE	FIELD BP	"BLIND" BP 50.7-268*-	PVT CELL BP	CALWLATED BP (EOS)	COMPOSITION
<pre>SM90-11 (Y-107) (Values Corrected to 8 Calc GOR (SCF/bbl): Measured GOR (SCF/bbl) Sample Specific Gravity:</pre>	13. 21 : 0.00	52.5	61. 7 a 88° 60. 1	44. 0 a 0'F 56. 0 a 80°F 47. 0 a 20°F 60. 0 a 100°F 50. 0 a 40°F 63. 0 a 120°F 55. 0 a 60°F 67. 0 a 140°F 72. 0 a 160°F	N2-0.24 n-U-2.85 C02-0.08 i-C5-1.6 CH4-0.51 n-CS-2.85 C2-0.46 C7+-83. i-C4-0.60 H2S-
(Y-221) (Values Corrected to 80 Calc GOR (SCF/bbl): Measured GOR (SCF/bbl) Sample Specific Gravity:	0.00 0.00	39.7 9 69° 41.4	⑤ ●	© 0'F a 80°F 0 20°F 0 100°F 0 40°F a 120°F a 60°F a 140° a 160°F	CO2- 1-C5- CH4- n-C5-
ANALYTICAL LAB: SPL	FI ELD BP	• BLIBD" BP	PVT CELL BP	CALWLATED BP (EOS)	COMPOSITION
<pre>SM90-09 (U-148) (Values Corrected to 8 Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:</pre>	: 0.00 : 0.00	101.8 a 72° 102.7	© •	© 0'F a 80°F a 20°F a 100°F a 40°F a 120°F a 60°F a 140°F	CH4- n-C5-
SM90-13 (U-119) (Values Corrected to 80' Calc GOR (SCF/bbl): Measured GOR (SCF/bbl) Sample Specific Gravity	4. 29 0.00	§ •	ග •	28.2 a 0°F 36.1 a 80°F 30.0 a 20°F 38.6 a 100°F 31.8 a 40°F 41.3 a 120°F 33.9 a 60°F 44.3 a 140°F 47,6 a 160°F	N2-0.17 n-U-3.3' i-c5-2.1 CH4-0.48 n-c5-3.3 C2-0.46 C6-5.0 C3-1.94 C7+-82.1 i-c4-0.81 N2S-
ANALYTICAL LAB: WEATHERLY	FI ELD BP	● BLIND" BP	PVT CELL BP	CALWLATED BP (EOS)	COMPOSITION
SM90-10 (WLC-004) (Values Corrected to 80° Calc GOR (SCF/bbl): Measured GOR (SCF/bbl) Sample Specific Gravity:	1.50 5.60	85.0 a 67' 85.7	€ •	34.0 a 0'F 39.0 a 80°F 35.0 a 20°F 41.0 a 100°F 36.0 a 40°F 42.0 a 120°F 38.0 a 60°F 44.0 a 140°F 45.0 a 160°F	N2-0.15 n-C4-3.1 CO2-0.03 i-C5-2.1 CH4-0.42 n-CS-3.5 C2-0.38 C6-7.3 C3-1.69 C7+-80. i-C4-0.71 H2S-
SM90-12 (WLC-047) (Values Corrected to & Calc GOR (SCF/bbl): Measured GOR (SCF/bbl) Sample Specific Gravity	0.00 5.00	85.0 a 67° 85.7	46.0 a 95° 44.5	a 0°F a 80° a 20°F a 100°F a 40°F a 120°F a 60°F a 140° a 160°F	CO2- i-C5- CH4- n-C5-
ANALYTI CAL LAB: RI PER	FI ELD BP	RI PER BP			COMPOSITION
SM90-12 (WLC-047) Neasured GOR (SCF/bbl):	78.0 a 88°	62. 4 a 72 °			N2-0.30 n-U-3.0 CO2-0.01 i-ES-0.0 CH4-0.26 n-C5-0.0 C2-0.09 C6+-0.0 C3-0.15 i-C4-0.03 H2S-

SPR Sulphur Hines 2-4-5 Pressurized Sampling

	Field Contractor:	CORE	Tool Type	: POSITIVE DISPLACEMENT TOO	
ANALYTICAL LAB: CORE	FIELD BP	MBL INDM BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
(Values Cormctad to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:	13.00 0.00	75.7 a 74° 76.9	76.7 a 74° 77.9	65.0 a 0°F 80.0 a 80°F 68.0 a 20°F 84.0 a 100°F 72.0 a 40°F 89.0 a 120°F 76.0 8 60°F 93.0 8 140°F 98.0 a 160°F	M2-0.38 n-U-3.; C02-0.10 i-a-2.1 CH4-0.67 n-C5-3.(C2-0.50 C6-6.! C3-2.02 C7+-80. i-U-0.82 M2S-
\$M90-49 (13112-E) (Values Corrected to 80°) Calc GOR (SCF/bbl): (Measured GOR (SCF/bbl): (Sample Specific Gravity:	0.00	44.7 a 98° 41.1	§ •	© 0°F & 80°F a 20°F & 100°F a 40°F & 120°F 8 60°F a 160°F & 160°F	N2- n-C4- CO2- i-C5- CH4- n-C5- C2- C6- C3- C7+- i-C4- H2S-
ANALYTICAL LAB: BPL	FIELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
(Values Corrected to 80°) Calc GOR (SCF/bbl): 3 Measured GOR (SCF/bbl): (Sample Specific Gravity:	3. 38 0.00	60.7 a 78° 60.9	§ •	23. 7 a 0'F 30. 7 a 80°F 25. 2 a 20°F 33. 0 a 100°F 26.9 8 40°F 35. 5 8 120°F 28.7 a 60°F 38. 3 a 140°F 41. 5 a 160°F	N2-0.14 n-U-3.1 CO2-0.08 i-Cs-1.9 CH4-0.38 n-C5-3.1 C2-0.43 C6-5.8 C3-1.82 C7+-82. i-U-0.76 H2S-
SM90-50 (13136-E) (Values Corrected to 80° Calc GOR (SCF/bbl): (Measured GOR (SCF/bbl): (Sample Specific Gravity:	0.00	a •	জ •	© 0°F & 80°F a 20°F & 100°F a 40°F & 120°F a 60°F a 140°F & 160°F	N2- n-C4- CO2- i-C5- CH4- n-C5- C2- C6- C3- C7+- i-u H2S-
ANALYTICAL LAB: WEATHERLY	FI ELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
(30-A) (Values Corrected to 80°) Calc GOR (SCF/bbl): 2 Nessured GOR (SCF/bbl): 6 Sample Specific Gravity: (2. 40 6.70	55.0 a 71° 55.9	70.0 a 95° 68.5	41.0 a 0'F 48.0 a W'F 43.0 a 20°F 50.0 a 100°F 45.0 a 40°F 52.0 a 120°F 46.0 a 60°F 54.0 a 140°F 55.0 a 160°F	N2-0.24 n-C4-2.7 C02-0.04 i-C5-2.1: CH4-0.45 n-CS-3. k W-0.29 C6-7.7 C3-1.39 C7+-80.1 i-U-0.67 H2S-
(Values Corrected to 80°) Calc GOR (SCF/bbl): (Measured GOR (SCF/bbl): 1 Sample Specific Gravity:	0.00	9 •	ହ •	a 0'F	N2- n-C4- CO2- i-C5- CH4- n-C5- F C2- C6- C3- C?+- i-C4- H2S-
	Field Contractor:	WEATHERLY	Tool Type:	RUSKA FLOW THRU TOOL	
ANALYTICAL LAB: CORE	FI ELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
Calc GOR (SCF/bbl): 1 Measured GOR (SCF/bbl): 0 Sample Specific Gravity: 0	13. 17).00	35.7 a 68° 37.5	45.0 a 78°	34.0 a 20°F 48.0 a 100°F 37.0 a 40°F 52.0 a 120°F 41.0 a 60°F 57.0 a 140°F 62.0 a 160°F	CO2-0.12 i-C5-2.05 CH4-0.59 n-C5-3.41 C2-0.46 C6-3.72 C3-1.84 C7+-84.1 i-C4-0.73 H2S-0.03
Calc GOR (SCF/bbl): (Measured GOR (SCF/bbl): (Sample Specific Gravity:	0.00	36.7 a 65′ 39.0		© 0'F & 80°F a 20°F & 100°F a 40°F & 120°F a 60°F & 140°F & 160°F	N2- n-U- CO2- i-C5- CH4- n-C5- C2- C6- C3- C7+- i-C4- H2S-

SPR Sulphur Mines $2\text{-}4\text{-}\mathrm{S}$ Pressurized Sampling

	Field Contractor	: WEATHERLY	Tool Type:	RUSKA FLOW THRU TOOL	
ANALYTICAL LAB: SPL	FI ELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-18 (V-9) (Values Corrected to 80 Calc GOR (SCF/bbl): Neasured GOR (SCF/bbl): Sample Bpecific Gravity:	6. 31 0.00	9	कु ●	38.9 a 20°F 46.1 5 80°F 41.2 a 40°F 51.7 9 120°F 43.6 8 60°F 54.8 9 140°F 58.2 9 160°F	N2-0.21 n-U-3.06 C02-0.08 1X5-2.33 CH4-0.73 n-C5-2.85 C2-0.42 C6-4.77 C3-1.64 C7+-83.2
Celc GOR (SCF/bbl): Nessured GOR (SCF/bbl): Sample Bpecific Grrvity:	0.00	101.2 a 73 •	ණ •	© 0°F & 80°F a 20°F a 100°F a 40°F a 120°F a 60°F a 140°F a 160°F	CH4- n-C5-
ANALYTICAL LAB: WEATHERLY	FI ELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-15 (WLC-042) (Values Corrected to 80°) Calc GOR (SCF/bbl): Neasured GOR (SCF/bbl): Sample Bpecific Grrvity:	1. 20 5.70	58.0 a 70° 59.0	44.0 a 95° 43.3	37. 0 a 0°F 44. 0 a 80°F 39. 0 a 20°F 45. 0 a 100°F 40. 0 a 40°F 47. 0 a 120°F 42. 0 a 60°F 48. 0 a 140°F 50. 0 a 160°F	N2-0.13 n-C4-2.6' C02-0.03 i-C5-1.9' CH4-0.46 n-C5-3.11 C2-0.29 C6-6.9' C3-1.39 c7+-82.4 i-cl-D.61 N2S-0.0'
SM90-17 (WLC-012) (Values Corrected to 80' Caic GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Bpecific Gravity:	0.00		क •	a 0'F	N2- n-C4- CO2- i-C5- CH4- n-C5- C2- C6- C3- C7+- i-C4- H2S-
ANALYTI CAL LAB: YI PER	FIELD BP	NIPER BP			COMPOSITION
SM90-17 (MLC-012) Measured GOR (SCF/bbl):	60.0 a 88°	69.4 a R'			N2-0.20 n-C4-0.0 C02-0.03 i-C5-0.0 CH4-0.30 n-C5-0.0 C2-0.10 C6+-0.0 C3-0.17 i-u-o.03 N2s-

SPR Sulphur Nines 2-4-S Prowrigad Sampling

	Field Contractor:	MICROGAGE	Tool T	ype: E	EVACUATED SAMPLER	
ANALYTICAL LAB: SPL	FIELD BP	"BLIND" BP	PVT CELL B	SP	CALWLATED BP (EOS)	COMPOSITION
SM90-68 (B-10) (Values Corrected to 80°		9 •	a	•	a 0' F a 80 a 20° F 8 100 8 40° F 8 120	°F CO2-0.03 i-C5-2.2 °F CH4-0.11 n-C5-3.8
Celc GOR (SCF/bbl): Measured GOR (SCF/bbl): Semple Specific Gravity:	0.00				a 60° F 8 140 8 160	
FIELD COMMENTS: He 3 1453	B pair					
ANALYTICAL LAB: WEATHERLY	' FIELD BP	"BLIND" BP	PVT CELL B	P	CALWLATED BP (EOS)	COMPOSITION
SM90-69 (B-11) (Values Corrected to 80°	a -	69 •	9	•	© 0'F 2 80 a 20°F 2 100 a 40°F 2 120	*F CO2-0.02 i-ES-2.1
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:	5.20				8 60°F a 140 a 160	°F C2-0.19 C6-8.9
FIELD CONNENTS: He 2 1453	pair					
	Field Contrrctor:	CORE	Tool T	ype: P	OSITIVE DISPLACEMENT TO	0
ANALYTICAL LAB: CORE	FI ELD BP	"BLIND" BP	PVT CELL B	P	CALWLATED BP (EOS)	COMPOSITION
SM90-53 (65A2127) (Values Corrected to 80°	175.0 a 99° 168.4	539.7 a 69° 544.1	339. 7 a 9 333. 1	3	13.0 a 0°F 351.0 a 80 24.0 a 20°F 358.0 a 100 34.0 a 40°F 365.0 a 120	•F E - K i-CS-1.9
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:	0. 00				43.0 a 60°F 371.0 a 140 376.0 a 160	-F C2-0.38 C6-6.9
\$490-54 (65A2156) (Values Corrected to &	67.0 B 94' 0°) 62.1	344.7 a 67° 349.9	69	•	a 20°F 2 10 0	
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:					a 40°F	40°F C2- C6-
ANALYTI CAL LAS: SPL	FI ELD BP	"BLI ND" BP	PVT CELL B	P	CALWLATED BP (EOS)	COMPOSITION
BWD-51 (61D\$3290) (Values Corrected to E Calc GDR (\$CF/bbl): Measured GCR (\$CF/bbl): Sample Specific Gravity:	: 0.00	9 •	69	•	a 40° F a 120	00°F CO2-
\$190-52 (61D\$2447)	70. 0 a 98 *	56.9 a 78°	69		~9.2 a 0°F 95.7 a 8 0	*F N2-0.76 n-c4-2.9
(Values Corrected to 80° Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:	8. 37 0.00	57. 7			90.9 a 20°F 97.3 a 100 92.5 a 40°F 99.1 a 120 94.1 a 60°F 101.0 a 140 103.1 a 160	°F CH4-0.37 n-c5-2.3 °F C2-0.41 c6-5.7
ANALYTICAL LAB: WEATHERLY	FIELD BP	"BLI ND" BP	PV7 CELL B	P .	CALWLATED BP (EOS)	COMPOSITION
\$\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	78.0 a 94° 0°) 75.9	196.0 a 70° 197.5	185.0 a 9 182.8		73.0 a 0'F 86.0 a BD0 76.0 a 20°F 89.0 a 100	*F CO2-0.06 i-C5-1.9
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:					79.0 a 40°F 92.0 a 120 83.0 a 60°F 95.0 m 140 98.0 m 160	°F C2-0.32 C6-7.3
\$190-56 (570\$1283) (Values Corrected to 8	42. 0 a 63'		69	•	೨೦ 0'F a 80 a 20°F 9 100	*F CO2- i-C5-
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Gravity:					a 40°F a 120 a 60°F a 1 a 160	40°F C2- C6-

SPR Sulphur Mines 2-4-S Pressurized Sampling

F	ield Contractor:	- UFATHERLY	Tool Type	RUSK4 FLOW THRU TOOL	
ANALYTICAL LAB: CORE	FIELD SP	"BLIND" BP	PVTCELL BP	CALCULATED BP (EOS)	COMPOSITION
\$M90-25 W-223) (Values Corrected to 80°)	90.0 a 88°	26.7 a 68° 27.9	37.7 a 88° 36.9	32.0 a 0° F 41.0 a 80° F 34.0 a 20° F 44.0 a 100° F 36.0 a 40° F 4r.0 a 120° F	N2-0.18 n-U-2.3 CO2-0.05 i-C5-?.0 CH4-0.32 n-K-2.3
Calc GOR (SCF/bbl): 13 Neasured GOR (SCF/bbl): 0 Sample Specific Gravity: 0	.00_			39. 0 a 60°F 51. 0 a 140°F 54.0 a 160°F	CH4-0.32 n-K-2.3 C2-0.43 C6-2.2 C3-1.68 C7+-87. 1-C4-0.61 H2S-
\$M90-26 (W-184) (Values Corrected to 80°)	88.0 a 82° 87.7	166.7 a 68° 172.7	⑤ ●	158.0 a 0'F 196.0 a 80°F 168.0 a 20°F 207.0 a 100°F 178.0 a 40°F 215.0 a 120°F	N2-0.71 n-U-2.5 CO2-0.36 i-C5-1.5 CH4-2.78 n-CS-2.2 C2-0.30 C6-4.2
Celc GOR (SCF/bbl): 0 Measured GOR (SCF/bbl): 0 Sample Specific Gravity: 0.	.00			188.0 a <u>40°</u> F 22L.0 a 140°F 232.0 a 160°F	C2-0.30 C6-4.2 C7+-83. i - Cc- 0. 64 H2S-
ANALYTICAL LAB: SPL	FIELD BP	"SLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
\$M90-22 (U-248) (Values Corrected to 80°)	85.0 a 91' 84.0	112.7 a 77° 113.3	a •	21. 3 a 0' F 27. 0 3 80° F 22. 5 a 20° F 28. 9 a 100° F 23. 9 a 40° F 31. 0 a 120° F	N2-0.14 n-C4-2.8 CO2-0.04 f-C5-0.2 CH4-0.29 n-C5-3.1
Catc GOR (SCF/bbl): 2. Measured GOR (SCF/bbl): 0 Sample Specific Grevity: 0	.00			25.4 a 60°F 33.3 a 140°F 36.0 a 160°F	C2-0.36 C6-5.2 C3-1.59 C7+-83. i - U- 0.66 N2S-
\$M90-24 (U-118) (Values Corrected to 80°)	100.0 a 91° 99.0	a •	§ •	8 0°F 8 80°F 8 20°F 8 1000°F a 40°F a 120°F	
Calc GOR (SCF/bbl): 0 Measured GOR (SCF/bbl): 0 Sample Specific Gravity:	.00			a 60°F 8 140°F 8 160°F	C2- C6- C3- C7+- i - u N2S-
ANALYTICAL LAB: WEATHERLY	FIELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-21 (ULC-142) (Values Corrected to 80°)	88.0 a 90°) 86.5	46.0 a 68° 47.2	38.0 2 95° 35.8	29.0 a 0°F 34.0 a 80°F 30.0 a 20°F 36.0 a 100°F 32.0 a 40°F 37.0 a 120°F	N2-0.15 n-C4-2.6 CO2-0.01 i-C5-1.9 CH4-0.17 n-C5-3.2
Calc GOR (SCF/bbl): 0. Measured GDR (SCF/bbl): 4. Sample Specific Gravity:				33.0 a 60°F 38.0 a 140°F 39.0 a 160°F	C2-0.22 C6-6.8 C3-1.17 C7+-83 i - U - O . 61 M2S-
SM90-23 (WLC-029) (Values Corrected to 80°)	85.0 a 91') 83.9	a •	ହ •	80°F 72.0 a 80°F 64.0 a 2D'F 75.0 a 100°F 67.0 a 40°F 78.0 a 120°F	M2-0.39 n-U-2.1 CO2-0.09 i-C5-2.0 CH4-1.47 n-C5-3.4
Calc GOR (SCF/bbl): 0 Measured GOR (SCF/bbl): 11 Sample Specific Grevity: 0	1. 60			70. 0 a 60°F 81.0 a 140°F 83.0 a 160°F	C2-0.17 C6-7. C3-1.09 C7+-80 i-cl-0.56 H2S-
ANALYTI CAL LAB: RI PER	FIELD BP	WI PER BP			COMPOSITION
SM90-21 (WLC-142)	88.0 a 90°	114. 4 a 72°			N2-0.49 n-C4-0. C02-0.02 i-C5-0. CH4-0.12 n-C5-0. C2-0.08 C6+-0.
Measured GOR (SCF/bbl): 13	3.07				C3-0.14 1-C4-0.02 H2S-

BPR Sulphur Nines 2-4-S Pressurized Sampling

SAPLE DEPTH 2950

Field Contractor: MICROGAGE

Tool Type: EVACUATED BAWLER

ANALYTICAL LAB: SPL	FI ELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-71 (B-12) (Values Corrected to 80°) Calc GOR (SCF/bbl):		35.7 a 80° 35.7	e •	8 D'F 8 80°F 8 20°F 8 100°F 8 40°F 8 120°F 8 60°F 8 140°F	u-o. 37 n-C4-3.1 C02-0.06 1-C5-2.1 CH4-0.39 n-C5-3.1 C2-0.43 C6-5.1
Measured GOR (SCF/bbl): Semple Specific trevity:	0.00			8 160°F	C3-1.75 C7+-82 1-C4-0.77 H2S-0.1
FIELD COMMENTS: VAC a 29.9) psia				
SM90-72 0-13) (Values Corrected • 80°)	9 .	36.2 a 80° 36.2	8 .	64.8 a 0°F 70.5 a 80°F 66.2 a 20°F R.1 a 100°F 67.6 a 40°F TJ.9 a 120°F	N2-0.54 n-C4-2.i C02-0.06 1-C5-1.i CH4-0.29 n-C5-2.i
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample specific Gravity:	0.00			69.0 a 60°F 15.9 a 140°F 78.1 a 160°F	C2-0.39 C6-5.5 C3-1.59 C7+-83. 1-C4-0.65 N2S-0.(
FIELD COMMENTS: VAC a 29.9	psis				
\$M90-73 (B-15) (Values Corrected to 80°)	a •	79.5 a 8 0° 79.5	т. •	14. 4 a 0°f 20. 2 a B0' F 15. 6 a 20°f 22. 2 a 100°f 16. 9 a 40°f 24. 4 a 120°f	N2-0.08 n-U-0.1 C02-0.05 i-c5-1.9 CH4-0.24 n-c5-2.4
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grevity:	0.00			16. 5 8 60°F 27. 0 a 140°F 2B. 9 8 160°F	C2-0.43 C6-4.7 C3-1.82 C7+-84. i-C4-0.83 N2S-
FIELD COMMENTS: Ne a 1450	psia				
ANALYTICAL LAB: WEATHERLY	FI ELD BP	"BLI ND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-75 (8-14) (Values Corrected to 80°)) a ·	Ø •	a .	a 0'F e 80°F a 20°F a 100°F a 40°F a 120°F	N2-0.03 n-C4-2.8 C02-0.03 -1-C5-2.1 CH4-0.16 n-C5-3.5
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grevity:	0.00 7. 30			8 60°F 3 140°F 8 160°F	Q-0.29 C6-8.0 C3-1.46 C7+-80. i-C4-0.68 H2S-
FIELD COMMENTS: Ne a 1450	psia				
	Field Contractor	· CODE	Tool Type	DOCUTIVE DICDIACEMENT TO	
ANALYTI CAL LAB: CORE	Field Contractor	: CORE • BLl ND" BP	Tool Type:	POSITIVE DISPLACEMENT TOO CALCULATED BP (EOS)	COMPOSITION
	FI ELD BP 5a. o a 83°			CALCULATED BP (EOS) 21. 0 a 0' F 3D. 0 a 80° F 23. 0 a 20° F 33. 0 3 100° F	N2-0.10 n-C4-2.9 CO2-0.06 i-C5-2.1
ANALYTICAL LAB: CORE M - 6 1 (837825-D)	FIELD BP 5a. o 3 83° 57. 6 12. 91 0. 00	• BLIND" BP	PVT CELL BP 41. 7 3 83 •	CALCULATED BP (EOS) 21. 0 a 0' F 3D. 0 a 80° F	N2-0.10 n-C4-2.9
ANALYTICAL LAB: CORE M - 6 1 (837825-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Heasured GOR (SCF/bbl):	FIELD BP 5a. o 3 83° 57. 6 12. 91 0. 00	• BLIND" BP	PVT CELL BP 41. 7 3 83 •	CALCULATED BP (EOS) 21. 0 a 0' F 3D. 0 a 80° F 23. 0 a 20° F 33. 0 3 100° F 25. 0 a 40° F 56. 0 a 120° F 27. 0 3 60° F 40. 0 a 140° F	N2-0.10 n-c4-2.9/ CO2-0.06 i-c5-2.1/ CH4-0.27 n-c5-3.3/ Q-0.40 C6-6.8/ C3-1.64 C7+-81.
ANALYTICAL LAB: CORE M - 6 1 (837825-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grrvity:	FI ELD BP 5a. o a 83° 57. 6 12. 91 0. 00 0.8583 FI ELD BP 78.0 a 94°	• BLIND" BP 36.7 a 76° 37.3	PVT CELL BP 41. 7 3 83* 41. 3	CALCULATED BP (EOS) 21. 0	N2-0.10 n-C4-2.9/ CO2-0.06 i-C5-2.1/ CH4-0.27 n-C5-3.3/ Q-0.40 C6-6.8/ C3-1.64 C7+81./ i-C4-0.72 H2S-0.2/ COMPOSITION N2-0.06 n-C4-3.2/ CO2-0.06 i-C5-2.1/
ANALYTICAL LAB: CORE M - 6 1 (837825-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grrvity: ANALYTICAL LAB: SPL SN90-58 (349113-D)	FI ELD BP 5a. o a 83° 57. 6 12. 91 0. 00 0.8583 FI ELD BP 78.0 a 94° 76.5 1.80 0.00	• BLIND" BP 36.7 a 76° 37.3 **BLIND** BP 59.6 a 78°	41. 7 83° 41. 3	CALCULATED BP (EOS) 21. 0	N2-0.10
M- 6 1 (837825-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grrvity: ANALYTICAL LAB: SPL SM90-58 (349113-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl):	FI ELD BP 5a. o a 83° 57. 6 12. 91 0. 00 0.8583 FI ELD BP 78.0 a 94° 76.5 1.80 0.00 0.8605	• BLIND" BP 36.7 a 76° 37.3 **BLIND** BP 59.6 a 78°	41. 7 83° 41. 3	CALCULATED BP (EOS) 21. 0	N2-0.10 n-C4-2.91 C02-0.06 i-C5-2.1! CH4-0.27 n-C5-3.3; Q-0.40 C6-6.8 C3-1.64 C7+-81.; i-C4-0.72 H2s-0.2 COMPOSITION N2-0.06 n-C4-3.2(C02-0.06 i-C5-2.1! CH4-0.31 n-C5-3.6; U-0.43 C6-5.4(C3-1.82 C7+-82.1 IX4-0.76 H2s-
ANALYTICAL LAB: CORE M - 6 1 (837825-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grrvity: ANALYTICAL LAB: SPL SN90-58 (349113-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Heasured GOR (SCF/bbl): Sample Specific Errvity: SN90-59 (349171-D)	FI ELD BP 5a. 0 a 83° 57. 6 12. 91 0. 00 0.8583 FI ELD BP 78.0 a 94° 76.5 1.80 0.00 0.8605 42. 0 B 82° 41. 8 0. 00	• BLIND" BP 36.7 a 76° 37.3 **BLIND** BP 59.6 a 78° 59.8	PVT CELL BP 41. 7	CALCULATED BP (EOS) 21. 0	N2-0.10
ANALYTICAL LAB: CORE M - 6 1 (837825-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): ANALYTICAL LAB: SPL SM90-58 (349113-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Errvity: SM90-59 (349171-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Measured GOR (SCF/bbl):	FI ELD BP 5a. 0 a 83° 57. 6 12. 91 0. 00 0.8583 FI ELD BP 78.0 a 94° 76.5 1.80 0.00 0.8605 42. 0 B 82° 41. 8 0. 00	• BLIND" BP 36.7 a 76° 37.3 **BLIND** BP 59.6 a 78° 59.8	PVT CELL BP 41. 7	CALCULATED BP (EOS) 21. 0	N2-0.10
ANALYTICAL LAB: CORE M - 6 1 (837825-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grrvity: ANALYTICAL LAB: SPL SM90-58 (349113-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Errvity: SM90-59 (349171-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Sample Specific trrvity:	FI ELD BP 5a. o a 83° 57. 6 12. 91 0. 00 0.8583 FI ELD BP 78.0 a 94° 76.5 1.80 0.00 0.8605 42. 0 B 82° 41. 8 0. 00 0. 00 FI ELD BP	• BLIND" BP 36.7 a 76° 37.3 **BLIND** BP 59.6 a 78° 59.8	PVT CELL BP 41. 7	CALCULATED BP (EOS) 21. 0	N2-0.10
ANALYTICAL LAB: CORE M - 6 1 (837825-D) (Velues Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grrvity: ANALYTICAL LAB: SPL SM90-58 (349113-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Errvity: SM90-59 (349171-D) (Values Corrected to 80°) Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific trrvity: ANALYTICAL LAB: WEATHERLY	FI ELD BP 5a. 0 a 83° 57. 6 12. 91 0. 00 0.8583 FI ELD BP 78. 0 a 94° 76. 5 1.80 0.00 0.8605 42. 0 B 82° 41. 8 0. 00 0. 00 FI ELD BP	*BLIND* BP 36.7 a 76' 37.3 *BLIND* BP 59.6 a 78' 59.8	PVT CELL BP PVT CELL BP PVT CELL BP PVT CELL BP 25.0 a 95°	CALCULATED BP (EOS) 21. 0	N2-0.10

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	Field Contracto	r: CORE	Tool Type:	POSITIVE DI SPLACEMENT TOO	
ANALYTICAL LAB: WEATHERLY	FI ELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
\$M90-60 (349164-D) (Values Corrected to 80° Caic GCR (\$CF/bbl): Measured GCR (\$CF/bbl): Sample Specific Brevity:	0.00	e •	π. •	a 0°F e 80°F a 20°F a 100°F a 40°F a 140°F a 60°F a 140°F	N2- n-C4- CO2- i-C5- CH4- n-C5- C2- C6- C3- C7+- i-C4- N2S-
	Field Contracto	r: WEATHERLY	Tool Type:	RUSKA FLOW THRU TOOL	
ANALYTICAL LAB: CORE	FIELD BP	"BLIND" BP	PV1 CELL BP	CALCULATED BP (EOS)	COMPOSITION
SW90-28 (U-133) (Values Corrected to 80°)		25.7 a 68° 27.5	m. •	e D'F e 80°F 8 20°F 8 100°F 8 40°F 8 1120°	CO2- 1-C5- F CH4- n-C5-
Calc GOR (SCF/bbl): Heasured GOR (SCF/bbl): Sample Bpecific Grevity:				9 60° F e 140° 9 160° F	F C2- C6- C3- C74- 1-C4- H2S-
SM90-31 (W-208) (Values Corrected to 80	65.0 8 82° 1) 84.7	25.7 a 68° 27.5	36.7 a 80° 36.7	25.0 e 0' F 34.0 e 80° F 27.0 e 20° F 37.0 a 100° F 29.0 a 40° F 40.0 a 120° F	M2-0.13 n-C4-2.1 CO2-0.05 -1-E5-2.1 CH4-0.29 n-M-3.5
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Bpecific Grevity:	0.00			31. 0 e 60°f 44. 0 e 140°f 48. 0 a 160°f	C2-0.43 C3-1.75 C782 i - u- o. 60 H2S-0.1
ANALYTI CAL LAB: BPL	FI ELD BP	"BLIND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
SM90-30 (W-444) (Values Corrected to 80°) Calc GOR (SCF/bbl): Heasured GOR (SCF/bbl): Sample Specific Gravity:	3. 65 0.00	п. •	п. •	26.9 e 0°F 34.0 e 80°F 28.5 e 20°F 36.2 a 100°F 30.2 a 40°F M. 6 a 120°F 32.0 a 60°F 41.3 a 140°F 44.3 a 160°F	N2-0.17 n-C4-2.0 C02-0.07 i-n-0.9 CH4-0.41 n-C5-2. C2-0.46 C6-5.1 C3-1.75 C7+-83 i-C4-0.68 H2S-
m - 3 2 (Y-239) <values (scf="" 80°)="" bbl):="" calc="" corrected="" gor="" grevity:<="" measured="" sample="" specific="" td="" to=""><td>0.00</td><td>76.7 e 68° 77.9</td><td>η •</td><td>0°F e 80°F 20°F 2 100°F 40°F 2 120°FF 260°F a 140°F 2160°F</td><td>CO2- 1-C5-</td></values>	0.00	76.7 e 68° 77.9	η •	0°F e 80°F 20°F 2 100°F 40°F 2 120°FF 260°F a 140°F 2160°F	CO2- 1-C5-
ANALYTICAL LAB: WEATHERLY	FI ELD BP	● BLl ND" BP	PVT CELL BP	CALCULATED BP (EOS)	COMPOSITION
\$M90-27 (Y-116) (Values Corrected to 80 Caic GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Specific Grrvity:	1. 20	47.0 a 70° 47.5	24.0 a 95° 22.5	32.0 a 0°F 37.0 a 80°F 33.0 a 20°F 39.0 a 100°F 35.0 a 40°F 40.0 a 120°F 36.0 a 60°F 42.0 a 160°F 43.0 a 160°F	N2-0.19 n-U-3.1 CO2-0.02 i-C5-2. CH4-0.29 n-6-3.1 C2-0.36 C6-7. C3-1.84 C7+-80 i-CC-0.79 H2S-
mm-29 (Y-149) (Values Corrected to 80	75.0 2 80°	80.0 a 68°	a .	п 0°F е 80°F 8 20°F 8 100°F 8 40°F е 120°I	co2- 1-c5-
Calc GOR (SCF/bbl): Measured GOR (SCF/bbl): Sample Bpecific Grrvity:				8 60°F 8 140°F	
ANALYTICAL LAB: NIPER	FIELD BP	WI PER BP			COMPOSITION
\$M90-29 (U-149) Measured GOR (SCF/bbl):	75.0 a 80° 4.79	61. 4 372°			N2-0.33 n-U-0. CO2-0.02 i-C5-0. CH4-0.20 n-C5-0. C2-0.10 C6+-0. C3-0.17 i-CC-0.03 H2S-

APPENDIX II.

Specifications for Physical Measurement of **Psat** for SPR Pressurized Samples

Due to a number of factors, it is relatively difficult to obtain accurate and precise measurements of saturation pressures of SPR oil. To increase the reproducibility of these measurements (precision) as well as the accuracy, the following steps are recommended for visual PVT cell saturation pressure measurements of SPR oil. If the saturation pressure is measured at different temperatures, the following would apply to each temperature at which the saturation pressure is to be measured.

Recent studies have shown that the reported measured saturation pressure is dependent on many factors. One such factor is the method used to make the P-V measurement of the bubble point, either expansion (expanding a one-phase (liquid) system to two-phase (gas-liquid)) or compression (compressing a two-phase system to a single phase system).

Because the compression method is more reliable, all physical bubble point determinations conducted on SPR samples should be conducted using the compression method. Other factors which will are addressed below include:

- 1. the size of the sample injected into the visual PVT cell,
- 2. the size of volume change used to move the system from two-phase to one-phase,
 - 3. the spacing of the volume changes during the compression process,
- 4. the method for determining whether the system has equilibrated after an induced volume change before accepting a pressure measurement,
- 5. the method of interpreting of the P-V data to obtain the saturation pressure at a given temperature, and
 - 6. operator consistency.

Sample Size for PVT Cell Measurement

The down-hole pressurized samples drawn from SPR caverns should be at least 600 ${
m cm}^3$ in volume. Each sample should be analyzed for composition as well as saturation pressure. Therefore, the 600 ${
m cm}^3$ sample should be split into two parts, 200 cm3 for the PVT cell, and the remainder for compositional analysis and other measurements.

Volume Changes and Spacing When Making P-V Measurements

Once a sample of at least 200 $\rm cm^3$ has been injected into the PVT cell, the system volume should be adjusted so that a two-phase system with a gas cap of at least 200 $\rm cm^3$ can be compressed to a one-phase system. When compressing the system, at least 8 pressure measurements must be made before the system becomes one-phase. The volume changes should be chosen such that the final 4 of these measurements (as the system approaches one-phase) are moderately close together (i.e. spaced approximately 5 $\rm cm^3$ apart). Once the system is one-phase, at least 4 more points should be taken at well spaced intervals (i.e. choose the volume changes such that the resulting measured pressures are spaced 50 - 100 psia apart).

Insuring Sufficient Equilibration

The amount of shaking of the system and the time allowed for it to equilibrate after the volume change and before the pressure measurement must be sufficient to ensure complete equilibration between measurements. The system should be rocked 25 times after each volume change and then a raw pressure reading recorded. The system should then be rocked another 25 times and the pressure checked with the preceding result. This process should continue until the pressure is unchanged by rocking.

P-V Data Interpretation: Obtaining the Saturation Pressure

The visual bubble point (saturation pressure) should be recorded and reported for the sample's PVT cell measurements. In addition, the P-V data should be plotted with a straight line drawn through the one-phase data and a curved line drawn through the two-phase data. The intersection of these two lines should be graphically interpolated and reported as the graphically determined saturation pressure. Finally, a Y-function analysis should be performed, with all raw P-V data and calculated Y-function data included with a plot of the Y-function vs pressure in the final report. The form of the Y-function to be used should be:

where P is the PVT cell pressure and V the absolute volume in the PVT cell (as opposed to the volume change); $P_{\rm s}$ is the saturation pressure, and $V_{\rm s}$ the saturation volume.

For the Y-function analysis to be most useful, the absolute volume of the PVT cell must be corrected for pressure dependencies, such as mechanical expansion of the cell (and/or the mercury if used to change the system volume) at higher pressures.

Operator Consistency

To reduce the dependence of the data and thus the measured saturation pressure on operator technique, the above measurements should be performed by one operator per sample. Thus one operator will make all of the P-V measurements for a given sample, at all temperatures.

Example of Final Report

An example of the required data, graphs, and reported values has been included in the desired format.

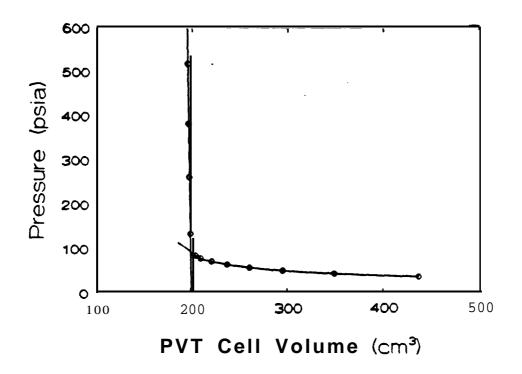
<u>Data</u> <u>Analysis Method</u>	<u>Saturation Pressure</u>
Visually Measured	80 psia
Graphically Interpolated	90 psia
Y-function	76.5 psia

Raw P-V Data and Y-function Analysis

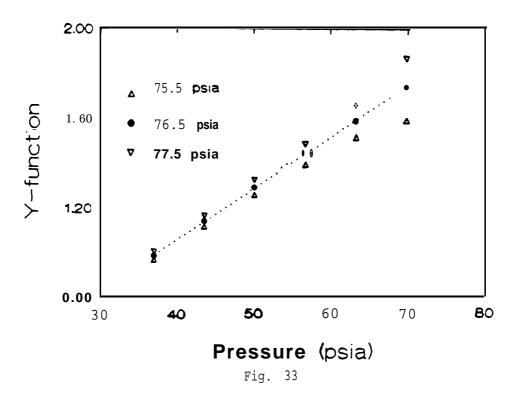
Compression P-V Data

Pressure (psia)	Volume of PVT Cell (cm³)	Calculated Y-function psat = 76.5 psia Vsat = 210.08 cm ³
37.09 43.57 50.14 56.71 63.29 69.86 76.43 83.01 132.15 260.05 379.98 516.02	436.95 349.55 295.86 261.13 237.78 221.60 210.13 205.00 199.63 198.04 196.99 196.05	0.98 1.14 1.29 1.44 1.58 1.73

PV Data for SPR Oil Sample



Y-function Analysis for SPR Oil Sample



REFERENCES

- Chung, T.H. and Burchfield, T.E., 1991, "SPR Gas-In-Oil Project", NIPER-518.
- Core Laboratories, 1875 Monetary Lane, Carrollton, TX 75006
- Digital Surveys, Inc., 10700 Corporate Dr., Suite 100, Stafford, TX 77477.
- Exline, P.G., 1937, "New Apparatus for Securing and Examining Sub-surface Samples of Oil", API Drilling and Production Practice, p. 126.
- Engineering Data Book, 7th Edition, 1957, Natural Gas Supply Men's Association, p. 161.
- Grandstone, P. and Cook, A.B., 1941, "Collecting and Examining Sub-Surface Samples of Petroleum", U.S. Bureau of Mines, T.P. 629.
- Guerro, E.T., 1959, A series of articles in Oil and Gas Equipment Vol. 5, No.
 5, March, pp.10-11, Vol. 5, No. 6, April, pp 10-11; Vol. 5, No. 7, May,
 pp. 16-17, Vol. 5, No. 8, June, pp. 16-17.
- Leutert Instruments, Inc., 5725 Hartsdale, Houston, TX 77036.
- Lindsly, B.E., 1934, "A Study of Bottom Hole Samples of East Texas Crude Oil", Report of Investigations 3212, USBM.
- Lindsly, B.E., 1936, "A Bureau of Mines Study of a Bottom Hole Sample from the Crescent Pool, Oklahoma", The Petroleum Engineer, Vol. 7, No. 5, p. 34.
- Linn, J.K. (Heffelfinger, G.S.), 1989, memorandum to E. E. Chapple dated July 24, 1989.
- Linn, J.K. (Heffelfinger, G.S.), 1989, memorandum to E. E. Chapple dated April 24, 1989.
- Linn, J.K. (Heffelfinger, G.S.), 1989, memorandum to E. E. Chapple dated May 15, 1989.
- Linn, J.K. (Heffelfinger, G.S.), 1989, memorandum to E. E. Chapple dated October 5, 1989.
- Microgage, Inc., 1990, Houston, Texas.
- Nath, J., Das, S.S., and Yadava, M.L., 1976, Industrial Engineers Chemical Fundamentals, Vol. 15, pp. 223-225.
- Preston, S.T. Jr., 1957, "Analysis by Low Temperature Distillation", Natural Gas Association of America, Tulsa, OK.
- Ruska Instrument Corporation, P.O. Box 630009, Houston, TX 77263-0009.

- Sclater, K.C., Stephenson, B.R., 1928, "Method of Obtaining Bottom Hole Data", Oil and Gas Journal, October 25, p. 114.
- Schilthuis, R.J., 1935, "Technique of Securing and Examining Sub-Surface Samples of Oil and Gas", API Drilling and Production Practice, Vol. 129, p. 120.
- Sonnier, Brian, This remark was made at the "Sulphur Mines Gas-In-Oil Project Meeting 3", July 18-20, 1990.

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Walas, S.M., 1985, Butterworth Publishers, p. 26.

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